DOCUMENT RESUME

ED 104 345 IR 001 734

AUTHOR	Roberson, David D.
TITLE	Revised Specifications for Uncoated Permanent/Durable Book Paper.
INSTITUTION	Barrow (W.J.) Research Lab., Richmond, Va.
SPONS AGENCY	Council on Library Resources, Inc., Washington, D.C.; Library of Congress, Washington, D.C.
PUB DATE	73
NOTE	126p.
EDRS PRICE	MF-$0.76 HC-$6.97 PLUS POSTAGE
DESCRIPTORS	*Books; Library Materials; Measurement; *Paper (Material); *Preservation; Publishing Industry; Testing
IDENTIFIERS	*Permanent Durable Book Paper

ABSTRACT

To aid in the evaluation of the physical qualities of books, specifications for permanent/durable book paper were developed and authenticated. Permanent/durable book paper was defined as paper suitable for use in the manufacture of books that meets or exceeds tests which demonstrate that it has an expectation of useful life under normal storage conditions of not less than 500 years. The literature was studied for material on factors affecting the longevity of paper and methods of testing permanence and durability. The resulting specifications include the minimum cold extraction pH, folding endurance, tear resistance, and retention of folding endurance after aging. Twenty commercially-available paper were tested by the study's methods. The test results are given in tabular form. A 211-item bibliography is appended. (Author/PF)

ED104345

REVISED SPECIFICATIONS FOR UNCOATED PERMANENT/DURABLE BOOK PAPER

Final Report on a Project

Jointly Supported by

The Library of Congress

and

The Council on Library Resources

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U.S. DEPARTMENT OF HEALTH, EDUCATION & WELFARE
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Richmond · Virginia · 1973

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Introduction

Paper has always been considered an insubstantial and ephemeral substance and yet there are paper materials in existence which have survived several centuries. There are also millions of books and countless paper records of relatively recent origin which cannot withstand even careful use. Though there have been many in the past who were concerned about the longevity of paper, it has only been within the last few decades that a growing understanding of its nature has produced an awareness that much can be done in the manufacture of paper to extend its service life.

For the user who needs long lasting papers, however, it is not enough to know that they can be made. Objective measures are needed which will permit evaluation and comparison of lasting qualities. Specifications based on the work of the late William J. Barrow and published in 1960 filled this need. The present purpose is to develop and authenticate a revised specification for Permanent/Durable book paper.

This report reviews literature on test methods and internal and external factors which affect paper longevity. It discusses experimental work with test methods and contains test data on thirty-two commercially available papers. These are the basis for the specifications.

The term Permanent/Durable should be reserved for papers with a high degree of strength and stability but the test methods described here will find application in evaluation of the lasting qualities of paper at all levels.

The authors wish to express their appreciation to the Council on Library Resources and the Library of Congress, both for the funding which made this project possible, and for their valuable advice and assistance in planning the work. We are especially grateful for the enthusiastic involvement of the late Verner W. Clapp.

I. Definition of a Permanent/Durable Book Paper

For the purpose of this project a Permanent/Durable book paper is defined as a paper suitable for use in the manufacture of books, whether as a printing paper or otherwise, that meets or exceeds tests which demonstrate that it has an expectation of useful life under normal storage conditions of not less than 500 years.

By "useful life" is meant the capability of sustaining normal careful use with constantly diminishing frequency, from 100 uses in the first year of life to 10 in the 500th.

The term "normal storage conditions" means freedom from exposure to direct sunlight, rain or snow; from attack by fungi or insects; and from damage by fire, water or smoke, with ambient atmosphere at the barometric pressures in which human activities are normally conducted, with the temperature normally at 70° F but not exceeding 100° F and with the relative humidity between 30 and 70%.

This definition represents the combined thinking of the late Verner W. Clapp of the Council on Library Resources, Frazer G. Poole of the Library of Congress and the Barrow Laboratory. It was accepted in June, 1971 as a point of reference for the execution of this project.

II. Factors Affecting Longevity of Book Papers

The length of a paper's useful life is determined both by the nature of the paper itself and by the conditions under which it is used. Some of the factors which fall into these two categories will be briefly considered.

The story of permanent/durable book paper, beginning early in the history of papermaking has been reviewed by Clapp (45). Williams (200) examined the problem of preserving deteriorating books and Smith (173) discussed history and research in the field of permanence.

Fiber

The basic structural element of paper is cellulose fiber. A variety of plant fibers is used for the purpose and their papermaking properties vary according to their source and treatment. The textile fibers, cotton and flax, have long been used in paper manufacture. The coarser bast fibers used in cordage also find use in paper. Beginning in the mid-19th century, the utilization of wood fiber has grown so that wood today is the major source of papermaking fiber. Paper has also been made from straw, sugar cane waste, esparto and numerous other materials.

Cotton and flax are naturally suited for papermaking because of their length, good strength and purity. Papers now in existence and in good condition after several centuries attest to the fact that long lasting papers can be made from them. The natural attributes which make this possible, however, may be destroyed or diminshed by the manner in which the fiber is handled. Paper made from rag which is badly degraded or cut to very short fiber length may not be any stronger or more stable than that made from wood pulp (19) even though the word "rag" has traditionally been associated with quality.

Wood pulp is prepared from wood by chemical and physical processes and combinations of the two. Chemical pulping involves the digestion of the wood with strong chemicals so that the non-cellulose constituents are removed from the cellulose fiber.

These non-cellulose materials, lignin, carbohydrates and rosin are generally thought to be harmful to paper's stability and they do not contribute to its strength. High-yield and semi-chemical pulping produce a greater weight of pulp from a given amount of wood by removing less of the non-cellulosics. Groundwood pulps are made by actually grinding wood. The process removes none of the lignin and it cuts the fiber to a relatively short length. Papers made with a high proportion of groundwood tend to be weaker. The chemical instability of groundwood pulp is particularly manifest by its darkening on exposure to light.

Longer fibers make stronger papers because they afford more opportunity for an individual fiber to be bonded into the sheet structure. This is one of the reasons for the strength of good cotton paper, but the fibers of textile grade cotton which may be up to several inches long are too long for good papermaking and must be cut to shorter length. Excessively long fibers tend to tangle and form clumps in the water suspension and produce a very non-uniform sheet. Wood pulp fibers are shorter than cotton, and hardwood fiber with an average length of 1-1.5 mm is shorter than softwood fiber which averages 3-4 mm in length. Even softwood fiber needs some cutting if it is to be used by itself but short hardwood fiber alone would not make a strong sheet (47).

Flyate and Ledvik (67) found that the more fiber was re-used, the weaker was the paper produced. They recommended that where maximum strength is desired the use of reclaimed fiber should be limited.

Short fibers also have their uses. They fill the spaces between the longer fibers and give the sheet greater uniformity of formation, smoothness of surface and opacity. Some of the permanent papers currently available are not notably durable because these properties have been enhanced by greater use of short fibers and fines.

Some tradeoff may be necessary, but the paper user should be aware when strength has been sacrificed.

Shatzkin (168) using some of Barrow's results, makes the point that more can be accomplished in prolonging service life of paper at the point of manufacture by making it neutral than by making it stronger. He further says that neutrality does not hurt important paper qualities but that production of paper with maximum strength, beside being more expensive, would be bad for opacity, ink receptivity, ease of binding and the feel of the finished book. Carhart (42) replies that greater initial strength would facilitate even faster book-production and that the use of high ink-drying temperatures creates a need for greater strength. He contends that "we should build strength into paper in such a way that other desirable factors are not compromised". This is a worthy objective and his experience indicates that it is an attainable one.

The lasting qualities of different pulps have been compared by several investigators. Belenkaya and co-workers (23) arranged the following fibers in decreasing order of resistance to ageing: cotton, flax, kraft, sulfite. Diaconescu and Petrovan (57) observed that cotton is more durable than wood and kraft pulp is more permanent than sulfite. Wilson and Hebert reported that during the time of their accelerated ageing study of 19 papers, 100% rag bond was superior in nearly all respects. Wilson also reported (204) that high grade rag and wood pulp papers stored at the National Bureau of Standards for almost 30 years indicate comparable stability for both types. Heinonem (81) found that neutral paper containing no rag was more permanent than acid (pH 4.5-5.0) Finnish archives papers containing 10 to 50% rag. However, many believe that under identical conditions good rag fiber is more permanent than other types.

Spirova and Flyate (178) say that paper from cotton pulp is more durable than paper from bleached kraft. Windahl (207) says rag will withstand more abuse and will therefore last longer where paper is to be handled, but where there is very little handling rag and chemical wood papers will deteriorate at about the same rate, reaching the point of unusability at the same time. However, it would appear that if rag is initially stronger and they both lose strength at the same rate it would take rag longer to reach unusability.

It has been often stated that pulps containing a high percentage of the very stable alpha cellulose are more resistant to ageing (108). Kathpalia (105) quotes Sutermeister and Torrey, who had examined Chinese papers 550 to 925 years old and European papers as old as 425 years, as saying their alpha contents were 64.7-87.3%. This indicates that however helpful a high alpha content may be, a good degree of permanence can be achieved without it. Very high alpha content pulps 90-99% do not make strong paper because there is less interfiber bonding.

Different chemical wood pulping processes produce pulps of different ageing characteristics. Soda pulp does not make strong paper. Kraft or sulfate pulping produces a stronger pulp than the sulfite process. Zagulyaeva (65) thought it likely that greater hydrolytic cellulose degradation which occurs in the acid sulfite process is one of the reasons sulfite pulp is weaker than kraft, which is cooked in alkaline liquor.

Non-cellulose wood constituents may have a harmful effect upon paper's lasting qualities. As Luner has noted (124), there is increasing use of pulps retaining more carbohydrates and lignin but there is not now enough information on their effect on paper permanence. Hemicelluloses, which hydrate more readily than cellulose, are valued in some papers because of the added strength they may give to a sheet, but

they also hydrolyze more readily than cellulose so that their strength contribution is not a very permanent one. Further, their acidic degradation products may hasten the deterioration of cellulose (40). Van Royen (193) noted that rag paper yellowing was slight and less accelerated by heat than other papers. He attributed this to the absence of hemicelluloses on the rag fiber surfaces. In spite of lignin's instability Wilson and Hebert (203) believed that, excepting reflectance retention, reasonably permanent papers could be made from neutral sulfite semi-chemical pulp and there have been reports of groundwood-containing papers with remarkable stability. Cardwell (40) concluded that high lignin content does not always cause impermanence but that the effect of bleaching upon residual lignin is important.

Pulp Preparation

Chemical pulping processes as normally practiced do not remove all the lignin present and subsequent bleaching is needed for further cleaning of fibers used in making of book paper. This bleaching can also affect the stability of the fiber itself. Carboxyl and carbonyl groups may result from bleaching. During accelerated ageing these promote color formation and adversely affect physical properties though the relations are not the same (40). Not all bleaching processes are equally damaging.

Bleaching with chlorine or chlorinated lime may be degrading (132). Spirova and Flyate (178) say that chlorine dioxide bleaching is less damaging than calcium hypochlorite on permanence and durability of cotton pulps. Usmanov et al (191) observed that chlorine dioxide bleaching was less degrading than sodium hypochlorite and that optimum conditions for chlorine dioxide bleaching are pH 4 at 40° C. Mehra (132) says that chlorine dioxide does not degrade the fiber at all provided pH is kept between 6 and 7. Flyate and Afonchikov (65, pp. 1-9) report that chlorine dioxide bleaching does not usually produce

subsequent yellowing unless the pulp has been strongly over-bleached.

Most fiber requires mechanical treatment before it is made into paper. Beaters and refiners are used to cut long fibered pulp and to mash and fray individual fibers in order to produce more surface area for interfiber contact and improve the matting ability of the pulp.

A small amount of beating produces papers with better tearing resistance, higher bulk, greater dimensional stability and opacity but well beaten pulps give higher tensile strength and folding endurance (132).

Barrow pointed out (17) that both tear resistance and folding endurance are necessary for durable papers. Since one may be traded for the other during fiber preparation, he set up a table of desirable initial tear values. This took into account basis weight and the relative deterioration rates of fold and tear and was designed to assure that the initial values of both were such that the paper would not become prematurely unusable in either respect. The purpose was to obtain maximum longevity from the natural strength of the fiber.

Strong fiber is needed for papermaking but apparently the maximum fiber strength is seldom, if ever, utilized. The number and strength of interfiber bonds are major factors in determining paper strength. Page (144) has offered a theory dealing with the contributions of fiber strength and bond strength. Bonding strength increased with heat-ageing and this effect was greater in sheets which initially had a high degree of bonding. This is taken to be a result of crosslinking. It appears then that excessive fiber shortening as well as too much hydration can reduce tear resistance and may make the sheet subject to early embrittlement.

Acidity

The damaging effects of acidity are generally recognized. Excessive acidity may come from paper constituents, inks (15, 17, 18) and air pollutants (92, 87). Pravilova (153) suggested that a pH requirement be included in specifications for printing papers because of its importance to permanence. Fauser (62) says the main cause of book paper degradation is acidity. Gluchowski (72) found low pH to be the most important influence on strength loss due to ageing. Residual chlorides were also important but average pulp degree of polymerization was less significant.

Wilson (205) thought that acidity level was probably the most important single permanence factor. He and Hebert (204) showed that stability could be roughly correlated with initial pH but because of other factors they did not expect a high degree of correlation.

Belen'kaya and co-workers (65) believed that pH was a more meaningful value than total acidity, determined by titration, as a measure of the effect of acidity upon permanence.

Extant copies of Collier's printed about 40 years ago on an alkaline paper are still in excellent condition (202) but Hudson (86) has noted that some 17th and 18th century rag book papers, though more acid than one would prefer, are still in good condition.

Dixson and Nelson (58) suggested that acidity developed during ageing may be an important factor in determining deterioration rate. Wilson and Hebert (203) found it more correlatable with permanence than initial pH value but Parks and Hebert (147) thought this might be because the acidity produced was the result rather than the cause of fiber deterioration.

Acids normally present in wood and those which result from pulp processing may contribute to a paper's overall acidity level (40).

Conservators of paper materials have developed a number of deacidification methods for protecting existing paper from excessive acidity. Materials suggested include aqueous solutions of calcium hydroxide, calcium and magnesium carbonates and bicarbonates (18), borax, barium and strontium hydroxides and carbonates (176), methanol solutions of barium hydroxide (65), methanol-Freon solutions of magnesium methoxide (176) and the vapors of cyclohexylamine carbonate (118, 130, 174) and other organic bases. Smith (174) presents a good review of deacidification techniques.

Windahl (207) and others point out that non-acidity discourages hydrolysis but that oxidation, though perhaps less damaging, is more likely under such conditions.

Szwarcsztajn and Maj (182) observed that breaking length decreases as the stock pH digresses from the neutral range (6.5 - 8.0). The greatest losses at a given pH occurred when aluminum sulfate was used. They concluded that the use of neutral sizes and elimination of alum will improve all properties except tear resistance.

Belaya (24) observed that sizing, with the accompanying reduction in pH, was harmful and that fillers increased permanence though they reduced mechanical strength. Nyuksha (55) noted that the introduction of rosin and alum resulted in a decrease of optical stability during heat ageing. Perl'shtein (149) reported that the change in relative contents of alpha, beta and gamma cellulose in heat-aged papers was more rapid in rosin-sized sheets and attributed this to acidification by alum.

Belenkaya and co-workers (65) demonstrated in a well controlled experiment that, whatever fiber is used, alum rosin sizing is harmful.

Szwarcsztajn (181) reported that by using a neutral sodium aluminate solution obtained from sodium hydroxide and aluminum sulfate as his rosin coagulant he was able to use calcium carbonate entirely in place of kaolin and get increased brightness and improved printability without changing other physical properties. It is to be hoped that the near neutral rosin-type sizes now available will lead to general improvement of rosin-sized papers though rosin sizing should not be used at all when maximum permanence is needed. Belenkaya and co-workers (65) believed that abietic acid and other rosin substances oxidize with the passing of time and are harmful.

Alkalinity

Thomas (187) allows that alkaline coatings on acidic base stock are not an ideal situation even though the composite pH is neutral or slightly alkaline but he offers natural ageing data to support his suggestion that this is a more stable sheet than an all acid paper.

While it is generally agreed that a moderate degree of alkalinity is good for permanence there is not agreement as to what is a suitable level of alkalinity. As noted before (207) oxidation is more likely under alkaline conditions. Slipka (172) said that a pH of 9.5 in the beater was optimum for rapid beating and strength development (except tear resistance). This suggests that at that pH there is some softening and an increase in flexibility. Pravilova and Istrubtsina (65) rejected calcium hydroxide and borax deacidification as too alkaline because they produced cold extraction pH's of 8.25 and 8.7 respectively. The three most stable papers evaluated in Part V of this report have pH's 9.2, 9.5 and 9.5. Because fewer alkaline papers are made the effect of alkalinity on paper permanence is not as well understood as that of acidity. There is need for more investigation in this area.

Inclusions

Sizing is necessary in book papers to improve printability and abrasion resistance and reduce absorbency. Tub sizing particularly may also improve tensile strength and folding endurance. The damaging effects of rosin sizing and the alum which it involves have already been discussed. There is little evidence that other sizing processes, as long as they are non-acidic, are harmful. Some of the newer synthetic materials appear to be particularly innocuous.

Starches, glues and natural gums which by themselves may do little harm can serve as nutrients for insects and microbial organisms. In this way they may make paper more vulnerable to damage.

Fillers add to the weight of paper but do not contribute to its strength. In this respect they are not good for durability. However, they are needed for their ability to improve smoothness, brightness, opacity, density and ink reception. Though their contributions to the finished paper are mainly physical, they are not entirely chemically inert.

Titanium dioxide and zinc oxide are photo reactive and there is some evidence that they may be harmful (124), though Heinonem (81), on the basis of experience with pretreated copy papers, suggests that zinc oxide has a beneficial effect upon permanence. Treiber (188) says that cellulose in contact with titanium dioxide may be significantly oxidized when irradiated with UV. Attempts have been made to reduce the effect upon rayon which has been delustered with this pigment. They have involved addition of stabilizing ions, shielding the pigment with protective coating and a boiling pretreatment of the pigment. Of the two common forms of titanium dioxide, rutile and anatase, rutile is the more stable. The importance of titanium dioxide in the ageing of paper and possible remedies have not been thoroughly investigated.

Calcium carbonate increases permanence of heat-aged papers (23, 81, 151, 204, 203). Alekseeva (2, 1) and Belaya (24) have reported that kaolin has a similar ability. Thomas (187) has re-told the story of Sutermeister's experiment with natural ageing of papers filled with clay and lime mud which dramatically demonstrated the value of calcium carbonate. This experiment began in 1901 but Thomas reports that the carbonate-filled paper was still in good condition in 1969 whereas its acid counterpart was so brittle it could not be handled.

Parks and Hebert (147) have suggested that alkaline salts which confer ageing resistance upon paper may do so, not by pH control, but by a stabilizing action of the cations involved. It is possible that such stabilization does occur but it is likely that this effect is in addition to - not instead of - the pH effect.

Optical brighteners are good absorbers of ultraviolet light and they may promote deterioration but the question has not been thoroughly examined (124). Dahl (49) found that fluorescent brighteners of the stilbene type did not affect cellulose viscosity loss for papers which were heat-aged or exposed to ultraviolet.

Water history

When wet cellulose fiber is dried a certain amount of irreversible shrinkage takes place and there is a loss of surface area and reactivity. For this reason never-dried pulps which go directly from the pulping operation to the paper making process make somewhat stronger and more flexible papers. This is one of the reasons that continued re-use of the same fibers results in paper of declining quality. Overdrying of paper may make it stiffer and less resilient. These factors are always at work in the paper making process and they deserve consideration, but their effect upon longevity is not so great as the effects of fiber type and preparation and the chemical nature of the paper.

Atmospheric conditions

Many factors which affect the service life of paper are external to the paper itself and quite beyond the control of the papermaker. These relate to the environment and manner of use.

Heat accelerates deterioration. Barrow (15) reported that a difference of 20° C in temperature would change the rate of deterioration by a factor of 7.5 and collective experience has shown that books kept at lower temperatures last longer. Hudson and Edwards (88) compared the paper properties of a book which had lain in the Antarctic nearly 48 years with that of two other copies of the same printing which were obtained secondhand in Glasgow and Manchester. They found that paper from the Antarctic copy was visibly and measurably brighter and stronger than that from the other two copies. Avoidance of heat is then a most important requirement for proper storage of books and paper records. Refrigerated facilities have been seriously proposed for rare and valuable materials and would no doubt be beneficial, though the choice of a storage temperature must also depend upon the cost of maintaining it, how frequently the materials are to be used and the human factors of comfort and convenience.

It is generally agreed that the moisture content of paper which is directly related to ambient relative humidity affects deterioration rate. Degradation is more rapid at higher humidities. Yabrova (159), Parks and Hebert (147), Luner (124) and many others report that heat ageing is faster under moist conditions than in dry ovens. The presence of moisture leads to hydrolysis of glucosidic linkages in cellulose and hemicellulose and probably accelerates the reactions of impurities (40). Smith (175) predicts that papers stored at 20-30% R.H. will last longer than if they were stored at 50% R.H.

On the other hand, moisture in paper lubricates it and reduces stiffness so that it is more pliant and less damaged by handling. Wessel (197) says the moisture content which is in equilibrium with 30% R.H. is about the lowest that is safe.

The possibility of maintaining different air conditions in storage rooms and reading rooms might be considered. There are some limits to this approach. If materials are to be kept at very low humidity to retard chemical deterioration they must be re-conditioned to a higher moisture content before they are used to prevent physical damage from handling. If materials are kept at low temperature, that temperature must not be below the dew point of the air in the reading room or moisture will condense on the material when it is brought from storage. If very low storage temperatures are desired, the material might be warmed to reading room temperature in a plastic envelope before being given to the user. Arrangements which require the user to wait while requested material is conditioned will not be popular.

A possible way of avoiding conditioning problems is to locate glove boxes or cuff boxes along a wall which separates the storage room from the reading room. This would permit the user to handle materials and read them through a glass window while they remain at the controlled temperature and humidity of the storage room.

While such drastic approaches may not be suitable for general application, the idea of keeping stack areas a few degrees cooler than the comfortable temperature of reading rooms is very sensible.

Air pollution has a deleterious effect upon paper (12). Hudson (86) demonstrated with 16th and 17th century books from two libraries exposed to different pollution

levels that atmospheric pollution does cause lower pH values, particularly at the edges of pages. Browning (36) lists sulfur dioxide, ozone and nitrogen oxides as harmful contaminants. Langwell (116) contended that the main reason for deterioration of paper was sulfur dioxide in the air. He suggested it was not damaging by itself but that in the presence of metallic paper impurities such as iron it forms sulfuric acid. Wessel (197) has said that nitrogen oxides may facilitate the oxidation of sulfur dioxide to sulfur trioxide which, with water, produces sulfuric acid.

Hudson et al (90, 92) using radioactive sulfur dioxide, found that air-borne sulfur dioxide can be picked up in quantities harmful to paper especially along the page edges. Edwards et al (59) found that relative humidity did not affect the long term pickup rate but suggested that lower moisture content would result in a higher effective concentration of the acid.

Nitrogen oxides from internal combustion engines, thunderstorms and volcanoes are always present in the air in varying concentrations. Ozone, which is an extremely strong oxidant, is produced from atmospheric oxygen by action of ultraviolet light and electrical sparking. One prolific source is electrostatic precipitators which may be used in air conditioning equipment for dust removal. An "ozone trap" containing oxidizable material might be devised for use after precipitators and possibly ultraviolet bactericidal lamps.

Light

Exposure to light degrades paper. Short wavelength ultraviolet is particularly damaging to paper but near ultraviolet, blue and violet also take their toll (197). Artificial light is not as harmful as sunlight, but the increased use of fluorescent lights has made

shorter wavelengths more common in libraries. Yamaguchi (211) observed that both hard and softwood kraft pulps exposed to intermittent ultraviolet light lost strength and chemical tests showed that they had been degraded. Wilson (205) says that the damaging effect of visible and ultraviolet is much less pronounced in the absence of oxygen and concludes that the reaction is most likely photoxidation. Kleinert (109) noted that active pigments used in the manufacture of regenerated cellulose accelerated the degradation caused by light but that this effect can be counteracted by the action of anti-oxidants.

Wiley and Cooney (198) found that the mono - and di-benzoyl derivatives of ferrocene reduce the rate of photodegradation of cellulose to which it is applied. These materials absorb light of wavelengths damaging to cellulose and dissipate the energy harmlessly. They appear to reduce direct photolysis as well as photosensitized degradation which results from radiant energy absorption by impurities. The possibility that such additives might be of value in book papers is worth exploring.

The darkening of groundwood-containing papers on exposure to light is a familiar experience, whereas papers made from very clean pulps may be bleached by light. In both cases however there is deterioration of strength properties. Window glass filters out the most energetic wavelengths of sunlight. In normal practice, paper is not usually exposed to light for extended periods. Desai and Shields (55, 54, 56) showed photo-degradation to be a surface effect. It appears then that keeping books closed and papers covered when they are not in use is the most meaningful way to reduce light damage. Of course other practical measures for reducing ambient light intensity should not be ignored.

Other Environmental Factors

For the present purpose "dirt" may be defined as any foreign substance which may come in contact with paper materials. The effect of dirt on these materials may range

from undesirable to very damaging. Air-borne dust particles darken the pages of a book, particularly at their edges, and make it unpleasant to handle. They may contain spores of bacteria or nutrients for their growth. Some very damaging chemicals can reach paper in the form of dust in industrial areas. The soiling of books from handling may involve almost any material which is normally handled by people. Food residues may be most harmful because they encourage fungus infestation. Dirt of various kinds may be conveyed to books by vermin. Elimination of vermin and providing a clean storage environment are the most effective measures for keeping paper materials clean. Food and drink should not be permitted in such areas and some libraries forbid smoking for the sake of cleanliness as well as fire prevention. The installation of suitable dust removal apparatus on air handling equipment is to be recommended.

Cleanliness will reduce the problem of fungi but cannot eliminate it. Fungi and their spores are ubiquitous (187). Zagulyaeva (65) reported that all the papers he studied could be infected by molds and damaged by them, though flax and cotton were vulnerable to fewer species than chemical wood pulps. Kraft papers were most susceptible. He surmised that the lower resistance of the wood pulps was due to the presence of hemicelluloses and lignin and the structure of the wood cellulose itself with its higher carbonyl and carboxyl content. The most resistant paper tested was made of cotton fiber and contained a high chalk content. He notes that the optimum pH values of nutrient media for fungi are mostly below pH 7.

Nyuksha et al (141, 142, 65) observed that sized papers were less resistant than unsized ones. They attributed acidity increase during ageing mainly to sizing and noted

that papers containing calcium carbonate were more resistant. However, Pravilova and Istrubtsina (65) working with chromatographic paper, concluded that buffering does not improve biological resistance.

Nyuksha et al (141, 142, 65) reported that aged papers were more vulnerable to the attack of fungi. His observation that stable paper can be made only from clean rags suggests that, at least initially, fungi derive more nourishment from the non-cellulose constituents. Beside paper, fungi may thrive on nutrients in leather and adhesives (197) which are also important to the integrity of books. Garland (70) observed that fungus susceptibility of starch-treated papers increased with increasing concentration of starch but noted that cellulose, starch, casein and glue are all relatively safe from fungus attack because under normal conditions their moisture content is too low for these organisms.

Regulation of moisture content is the most effective fungus control measure. Wessel (197) says there is little growth below 70% relative humidity. Others recommend that for good protection the relative humidity should not be allowed to exceed 65%. Avoidance of localized high humidity conditions is facilitated by spacing shelving to permit free circulation of air. When a large mass of paper is stored in an area its total absorptive capacity is so great that individual items will not acquire a dangerous moisture content during brief periods of high humidity.

Control of fungi in paper by temperature manipulation is not practical (197). They may be dormant outside their growing range but some are killed only by temperatures around 200-250° F and, in most cases, cyclical freezing and thawing.

Petrova and his co-workers (177) have explored the possibility of disinfecting books with high frequency electromagnetic fields and found the idea promising, but the recommended process involves keeping the book at 90° C for 10 minutes.

Belaya (150 pp. 141-148) reported that a bactericidal lamp can, in 15 seconds, kill 60 to 80% of the organisms in air. The cover of this lamp absorbs the ozone-producing wavelengths so that this should not be a serious hazard in its use. Because the light from it is harmful to paper, an uncovered lamp should never be used in a room with books, but it may be used inside air circulation equipment. Belyakova (150 pp. 228-231) reported that in 30 minutes a circulating device using such a lamp killed 98% of the spores in a room containing 60 m^3 of air.

Numerous biocides have been used to kill fungi in paper. Though they do not afford the degree of protection to be had by control of relative humidity they are useful in tropical areas and where air conditioning is unavailable or inadequate. A popular fungicide for the purpose is thymol. It may be used as a fumigant or in interleaving material but it does not last indefinitely. Rybakova (150 pp. 29-46) offers recommendations for the use of formalin as a fumigant but indicates that complete destruction of molds is unlikely because of the difficulty of getting it throughout a book in sufficient concentration. Other materials which have been used are salicylanilide, phenyl mercuric nitrate, pentachlorophenol, beta-naphthol and para-nitrophenol. Schwarcz and Beiter (165) have patented a process in which objects are treated with a material which protects them by the controlled release of organotin compounds.

Solutions of mercuric chloride and thymol have been applied to book bindings. Belyakova (150 pp. 212-221) recommends the use of pentachlorophenate as an antiseptic for glues and says that beta-naphthol and trichlorophenate lose their effectiveness with increased humidity. Phenyl mercuric acetate, phenyl mercuric borate and borax are recommended for starch paste in the tropics.

Nyuksha et al (141, 142, 65) thought the addition of fungicides in the manufacture of paper showed promise of conferring good resistance to fungi. Garland (70) identified three effective agents but none of them could be applied during paper production because they were insoluble in water. He recommended experiments with water-soluble fungicides. Zagulyaeva (65) mentions the use of water-soluble sodium salts of chlorinated phenols, copper pentachlorophenate, salicylanilide, mercury compounds, arsenic compounds and some organic metal salts in the manufacture of paper. Stergiu et al (179) made cellulose highly resistant to degradation by light and soil micro-organisms by reacting a copper-cellulose complex with rhodanine.

Insects may be attracted to books by adhesives, sizing materials and other components of the book itself as well as by food and food wrappers left in them by readers. In most areas they may be controlled fairly easily by cleanliness, periodic inspection and awareness of the problem and they can be eradicated by fumigation and with insecticides (197).

Insects may live and breed in many places other than books themselves. Some possibilities are ventilation ducts, rat holes, holes in walls for the passage of pipes, cracks around door and window frames, rotten wood and secluded spots under shelves where dust and debris may collect. Petrova (150) states that there are relations between storage conditions and the insect species present in a collection and suggests that control would be facilitated by a better understanding of them.

Wessel (197) and Petrova (150 pp. 18-28) recommend that all library acquisitions of uncertain history be examined and treated to destroy biological agents before they are added to the collection.

Formalin fumigation, while useful, does not always penetrate books in sufficient quantity, even in a fumigation chamber, to kill all insects and eggs. A measure of insect

control may be achieved with DDT without putting it into the books themselves by applying it to surfaces in the storage room where insects may come in contact with it. The toxicity persists for a long time on impervious surfaces but the presence of such a film is not attractive. Formalin and beta-naphthol which may be added in small amounts to starch pastes as fungistats do not poison insects. DDT is effective as an intestinal poison in flour paste in concentrations as low as 0.1% but its possible reactions with other additives are not known (150). In the tropics, books are sometimes immersed in gasoline for insect control.

Rats and mice are to be avoided in libraries, not only because of their direct damage to books, but because their presence encourages insect infestation. Rodents may gnaw the bindings of some books for food and their use of shredded paper for nesting materials makes them most unwelcome. Clean libraries which offer them no food and difficult access will suffer little harm from rodents. Where they are a problem, traps and poisoned bait are usually quite effective.

Human beings present serious hazards to books and paper records. Hudson and Eynon (89) observed that the lactic acid of perspiration is harmful to sizing, though papers sized with alkyl ketene dimer and gelatin maintain their sized qualities better than those sized with rosin or starch. This is important even in a finished book because it makes the pages less easily soiled. Handling books with dirty hands and the leaving of food crumbs and wrappers in them are common problems. Probably the most serious damage inflicted by humans is the physical injury which results from carelessness and simple abuse in handling.

Recommendations for Future Research

Better understanding of the following areas would result in papers having longer service life and improved preservation methods.

1) Additives and treatments to reduce photodegradation

2) Effective economical and safe fungicides for application in manufacture and to existing papers.

3) Photo-activity of fillers.

4) Permanence level of high yield pulps and their effect on other pulps. Possible improvements.

5) Oxidation and the use of antioxidants in paper.

6) Determination of level at which alkalinity becomes harmful.

7) Practicality of dual air conditioning arrangement whereby materials are stored at lower temperatures than those maintained for human comfort in reading rooms.

8) Maintenance of maximum paper strength without sacrificing printability and aesthetic considerations.

Recommendations for Manufacture of Long-life Papers and Long-term Preservation of Papers

Manufacturing

1) Omit or reduce titanium dioxide in paper or protect against its photo effect.

2) Avoidance of iron contamination which may promote cross-linking, sulfuric acid formation and yellowing.

3) Neutral Sizing.

4) Calcium carbonate filler.

5) Long strong undegraded fiber beaten to a degree which gives both good folding endurance and tear resistance.

6) Cold extraction pH between 7.0 and 9.5.

7) Chlorine dioxide bleaching.

Preservation

1) Avoidance of relative humidities above 65%.

2) Avoidance of relative humidities below 35-40% if materials are to be handled.

3) Air conditioning equipment to provide lowest practical temperatures and circulation of air free of harmful pollutants and dust.

4) Shelf spacing to facilitate air circulation.

5) Prohibition of eating and smoking in stack, storage and reading rooms.

6) Routine inspections for evidence of mold, insects and rodents and appropriate prevention measures.

7) Reduction of ultraviolet light. Low intensity lighting in little-used storage areas.

8) Deacidification of excessively acid materials.

III. Permanence/Durability and its Evaluation

Since the publication of W. J. Barrow's "Tentative Specifications for Durable, Non-coated Chemical Wood Papers" (43) in 1960 much work has been done to improve our knowledge of what makes a long-lasting paper and how papers may be tested for these properties. The purpose here is to review some of this work, consider how it might apply to the writing of paper specifications and find some guidance for future efforts.

The literature has been examined by others and the reviews of Colpe (46), Neimo (135), Luner (124) and Cardwell (40) are particularly recommended. The collections of abstracts compiled by the Institute of Paper Chemistry (39, 196) are quite useful.

One cannot usefully evaluate the lasting qualities of a book paper by actually waiting for the end of its service life under normal use conditions. Various accelerated ageing methods are used in attempts to duplicate in a short time the natural deterioration which would occur over many years. Because of this, much of what has been written and said about the factors affecting paper longevity has been based on results, both chemical and physical, from accelerated ageing tests. Therefore an examination of them and the factors which affect their results is in order.

Heat Ageing

It is known that papers deteriorate faster at increased temperatures. Barrow (15) reported that a difference of 20° C in ageing temperature would change the rate of deterioration by a factor of 7.5. Others have reported comparable values. This temperature effect is the basis of most accelerated ageing of paper.

The rate of deterioration at any temperature is determined by measuring the change in some paper property with time. First order kinetics seem to be best for general application (36). This produces a linear relation when the log of the measured property is plotted against ageing time and the slope of this line, called the rate constant, k, is a measure of the reaction rate.

If a straight line results when the logarithms of the rate constants for several temperatures are plotted against their respective inverse absolute temperatures, the Arrhenius relation is said to apply and activation energy is independent of temperature. With such a plot it is possible to predict deterioration rate at normal temperature from those determined at elevated temperatures.

Browning (36), Gray (77), Luner (124) and others have noted that this method is strictly legitimate only if both the rate plots and the Arrhenius plots are linear. However, in spite of the necessary simplifying assumptions, procedures based on these principles are commonly employed because of their convenience and the lack of a clearly better way. Browning points out (36), "The changes of a paper property with time are not determined by any single chemical reaction whose effects can be isolated and controlled. Hence, applications of conventional kinetic treatment to ageing data on paper are largely empirical".

It has been noted by several (37, 124) that rate plots are not always linear. Luner (124) and Cardwell (40) say that in extensively aged samples much fiber failure occurs upon folding but in unaged or slightly aged papers bond failure is more likely. This changing mode of failure may be a reason for the non-linear plots sometimes obtained of log fold vs time.

Gray's lines for deterioration at a given temperature are straight (77). Though they are not presented he does give correlation coefficients and reports that there was no indication the relations were anything but linear on semi-log coordinates.

Considering the complicated nature of the question it would not be surprising if the activation energy did vary with temperature, but Arrhenius plots are usually linear. It has been suggested that the resulting activation energy is an average for several simultaneous chemical and physical processes (124, 40).

As the heat-ageing method is often applied, papers are aged at only one elevated temperature and their relative stability at room temperature is judged from the results. When this is done the assumption is being made that the deterioration rates for all papers are increased to the same degree by the same increase in temperature. If Arrhenius plots were developed in such a situation the lines for various papers would all be parallel or have the same slope. This would mean that the activation energies for their deterioration were all the same.

Gray's work (77) indicates that not all papers have the same activation energy for the loss of a particular property during heat ageing. In this situation it is incorrect to assume that the relative deterioration rates of a group of papers are the same at normal temperatures as at the prescribed elevated temperature. Millett (134) has pointed out that if the Arrhenius plots for two different papers intersect between the higher experimental temperature and normal temperature, the paper having the greatest apparent stability at elevated temperatures will actually be less stable under normal use conditions. On these grounds Gray (77) has objected to the TAPPI accelerated ageing method (185) which requires ageing at only one temperature. He contends that determination of the activation energy or temperature dependence of deterioration rate for each paper from the Arrhenius relation and multi-temperature ageing permits the most accurate estimation of deterioration rate at room temperature but notes that such an approach is impractically

expensive for routine permanence evaluation.

Even when rate plots are linear and the full Arrhenius approach is used there is a degree of uncertainty. Luner sees the accuracy required in determination of the rate constant k as a drawback. Millett and co-workers (134) stated that reaction rate is so dependent upon temperature that determination of rate with a 1% error demands temperature control of about ± 0.1° C. They have built ovens with very precise temperature control. Temperature uniformity within these ovens is maintained by forced air circulation.

Browning and Wink (37) have said that if the deterioration rate plot for a paper is known to be linear only one heat aged point is needed for comparison with data on unaged samples. But if linearity cannot be assumed for all papers as they suggest, multi-point testing would be required for any paper being tested for the first time. Further, if the deterioration is linear (on semi-log coordinates) the slope of the line can be more accurately determined on the basis of several points.

Barrow (13) described a graphical procedure employing a planimeter for establishing the best straight regression line according to the least squares method. This approach is uncomplicated and adequately accurate, but with the better electronic calculators available today, it is possible to do the same job faster and with greater accuracy using the classic least squares formulae. Programmable calculators and computers, where available, offer even greater speed.

Activation Energies

Millett and co-workers (134) determined activation energies for thermal degradation of unsized, unbleached kraft paper to be from 25.5 to 27.5 k cal/mol. On sized paper the value was 20-24 k cal/mol.

The Barrow Laboratory (22) has found activation energies of 22.7-33.0 k cal/mol, averaging 25.7 k cal/mol for loss of folding endurance and tear resistance at temperatures between 38° and 125° C.

Browning and Wink (37) calculated activation energy for deterioration of their samples which gave linear log fold vs time plots to be 29.5 k cal/mol. For the papers which did not give linear plots they plotted fold vs time $^{-2}$ at each temperature. This gave an almost straight line from which a rate constant was calculated and the Arrhenius relation was used to determine energies of activation of 31.4 to 35.5 k cal/mol. They applied the same methods to zero-span results and observed that loss of strength was small during the periods used and data was rather dispersed but trends were consistent. Calculated energies of activation were 26.7-28.9 k cal/mol.

Browning and Wink concluded that "prediction of permanence by accelerated ageing as performed in (their) work (37) appears to be justified in principle." Their Arrhenius plots were approximately linear and they suggested that activation energies for deterioration of a paper, whether determined by fold, tensile or specific absorption test methods are probably the same. While admitting that the deterioration rates of different papers may be affected differently by increasing temperature they, like Gray, recognized that using the complete Arrhenius approach on each paper is impractical and suggest that single-temperature ageing under moist conditions assuming a working value of 30.0 k cal/mol for activation energy is the best method presently available.

Van Royen (193) believed that the reactions occurring at 100° C were not significantly different from those at normal temperatures. He plotted the Arrhenius relation for the yellowing, folding endurance loss, and cellulose fluidity increase of four papers aged at temperatures from 80° to 160° C. Though the papers were of such diverse materials as straw, hardwood, softwood and rag fiber he obtained essentially parallel lines for these

tests and this assured him of the validity of Rasch's one-temperature ageing test, -- 3 days at 100° C (158).

Natural-Artificial Ageing Equivalency

If a one-temperature ageing test is to be used it is necessary to know the relation between natural long-term ageing and accelerated ageing. Van Royen (193) concluded that 3 days at 100° C is equivalent to 28 years of natural ageing. Wilson, who carried on Rasch's work, produced data giving a value of about 20 years (new rag 18.5, sulfite 20.5) by comparison with a group of papers which had naturally aged 26 years (201, 166, 159). Barrow (15) set the figure at 26 years and used a value of 25 for convenience in estimation. The average activation energy 25.7 k cal/mol obtained by the Barrow Laboratory since then (22) for dry oven ageing translates into an equivalency of 68 years natural ageing for 3 days at 100° C. The 30.0 k cal/mol activation energy proposed by Browning and Wink (37) for moist ageing would make 3 days at 100° C equivalent to 306 years.

Effect of Light

The damaging effect of light upon paper has also been employed to accelerate its deterioration. Spirova and Flyate (178) observed that changes caused by U-V radiation are about the same as those caused by thermal ageing. Desai (53) reports that wet strength of papers exposed to U-V increases like that of heat-treated pulp. Launer (119) has raised the question whether some of the damage attributed to light may actually be caused by resulting heat. Luner (124) notes that decomposition products of photolysis and low temperature pyrolysis of cellulose are similar. He suggests that photochemical degradation with its likeness to thermal degradation may be useful in place of or in addition to heat ageing. Though this appears to be a possibility, there seem to be no prescribed procedures for such a method nor has the rate of light-induced ageing been related to that of normal ageing.

It has been suggested (197) that photodegradation of cellulose is due to oxidation by oxygen or ozone and initiated by ultraviolet light. Rozmarin et al (163) proposed that photodegradation is a two-step process consisting of oxidative decrystallization followed by depolymerization. Wilson (205) says the damaging effects of visible and UV light are much less pronounced in the absence of oxygen and thereby concludes that the reaction is most likely oxidative.

Bleaching sometimes results from exposure to light (124). MacClaren et al (125) tells how reflectance of commercial paper samples exposed to UV at first increased, then decreased at a rate which depended upon relative humidity. Very dry samples continued to increase in reflectance even after 1500 hours of exposure. Desai and Shields (55, 54, 56) observed that filter paper exposed to UV yellowed more rapidly in the absence of moisture but that moisture had little effect upon scission of the cellulose chain. Their work shows photodegradation to be a surface effect. Paper exposed on one side to UV showed marked degradation on the exposed side and very little on the unexposed side.

LeNest and Silvy (121) report that micrographs of papers exposed to the whole xenon lamp spectrum showed surface erosion. Extended exposure of regenerated cellulose to UV in the 2300-3000 A range caused complete disappearance of the sample.

Reine and Arthur (161) investigated the effects of near UV (ca. 3500 A) on cotton cloth at 50° C. They observed significant losses in tensile and DP and increases in carbonyl and carboxyl content due to direct photolysis. The formation of carboxyl groups and the number of chain cleavages were correlatable. However, at 2537 A the loss in tensile was 5.6 times greater and the carboxyl content was over 400 times as great. Though the shorter wavelengths are much more damaging than the longer ones, near UV is certainly not harmless. Blue and violet light also affect paper adversely (197).

Similarities in degradation produced by heat and light (128, 124) have given impetus to search for free radical mechanisms. Kringstad and Lin (114) have shown that free radicals are involved in the near UV photodegradation of lignin. Kubat et al (115) demonstrated that presence of the radical scavenger hydrazine made mildly bleached and unbleached pine pulp more resistant to gamma radiation.

Chemistry of Deterioration

The factors which determine the permanence of paper are not well defined because there is not yet a thorough systematic knowledge of the chemical reactions involved in its deterioration. The picture is a variable and complex one involving many interactions. It is sometimes suggested (124) that investigations should begin with the ageing qualities of pulps alone to avoid the complications arising from the multitude of constituents which may be found in finished paper. Flyate and Afonchikof (66) outlined what appears to be a very well organized program to evaluate the effect of a number of factors on the permanence of papers made from four different pulps. Blank and co-workers (29) showed that in evaluating restoration methods aged papers should be used rather than new ones. They observed different responses to water washing, chloramine T bleaching and buffering with calcium and magnesium carbonates for the same papers before and after heat ageing. All three processes gave better results when applied to aged papers.

Hydrolysis of the cellulose polymer has for some time been considered a major cause of paper deterioration and various oxidative reactions have been thought to contribute. Crosslinking which may begin with oxidation but affects paper properties in its own specific way merits increased attention. A better understanding of the chemistry of degradation is needed.

Venter (194) studied the influence of eight factors on paper permanence and concluded that hydrolysis of polysaccharides was the only degradation mechanism at work under his ageing conditions.

Major (128) quotes a variety of views on the relative importance of hydrolysis and oxidation. Degradation of cotton yarn is oxidative rather than hydrolytic at 110-150° C in air at 40% RH (Conrad et al). Primary degradation reactions of viscose rayon are hydrolysis below 140° C, air oxidation between 140° and 160° C and destructive distillation above 160° C (Agster). Cotton degradation is primarily oxidative above 200° C and hydrolytic below 180° C (Haas). At 150-170° C strength loss is proportional to temperature and amount of moisture present and oxygen consumption is a function of the amount of moisture present (Waller, et al). Major concluded from his own work that in dry ageing in presence of oxygen at 170° C degradation is primarily a result of oxidation.

Wilson et al (201) observed that in both natural ageing and heat ageing there is an increase in acidity, but Phillip and Baudisch (151) found that the relative carboxyl contents of different celluloses are not changed by thermal treatment. They also found carboxyls located preferentially, but not exclusively, in the regions of lower order. With increasing carboxyl content thermal stability is decreased.

Hydrolysis

Hydrolysis causes decreases in chain length of the cellulose polymer by random breaking of the chains. The extent to which it occurs depends, according to Browning (36), upon concentration of acidity. Ivanov et al (98) found that hydrolytic degradation of cellulose by carboxylic acids is determined by hydrogen ion concentration while the nature of the acids is relatively unimportant.

The acidity which may be present in papers as a result of the processes and materials used in their manufacture is a major factor in hydrolysis of cellulose. The degradation products of both cellulose and hemicellulose, which hydrolyzes more readily, may increase the acidity of a sheet and promote further degradation (40).

It is known that acidity promotes hydrolysis of cellulose at normal temperatures (36), and is generally believed that alkaline hydrolysis occurs only under the severe conditions of some pulping processes. It is not known to what extent hydrolysis contributes to degradation of neutral or alkaline papers in dry ageing ovens where water is not plentiful.

Bleshinskii and Vinogradov (30, 31) have proposed a mechanism for high temperature (180-250° C) acid-free hydrolysis of cellulose in liquid medium. Its relevance to paper under natural and heat-ageing conditions is not known. They mention the possibility of hydrolysis with the direct participation of the hydrogen ions of water.

Shimazu and Sterling (169) observed that cellulose immersed in water under nitrogen at 100° C and 150° C hydrolyzes less than if it were heated to the same temperature in the absence of water. They suggest that if the degradation involves free radicals produced by heating, these are quickly quenched when water is plentiful.

Diaconescu and Petrovan (57) believed chemical decomposition of cellulose involved mainly hydrolysis of glucosidic links, regardless of pH, and that reactivity of glycosidic linkages increases with the introduction of OH, CO and COOH groups into the anhydroglucose unit.

Ivanov et al (100, 99, 113) have suggested that open rings make nearby glucosidic linkages more vulnerable to acids and propose that a treatment which would reduce or prevent ring opening would improve stability. Daruwalla and Narsian (50) found little experimental evidence to support the idea of acid-sensitive linkages that are more vulnerable than the normal 1:4-beta-glucoside linkage.

Ishikawa (95) and Shafizadeh (167) discussed cellulose structure as it relates to hydrolysis. Odintsov and Maraschenko (143) discussed the effect of cellulose adsorption of sulfuric acid upon hydrolysis. Much work has been done on the effect of strong acids on

cellulose. Higgins et al (85) suggested that if rate of hydrolysis were being modified by physical processes (such as diffusion) one would expect a reduction of activation energy, but activation energy goes up for crystalline regions and they attribute this to the fact that hydrogen bonds must be broken in addition to glucosidic bonds. Preferential attack on more accessible bonds causes the rate constant to decline as the reaction proceeds.

Higgins (84) determined mean activation energy for homogeneous cellulose hydrolysis to be 28.3 k cal/mol. Nota La Diega (139, 137, 138, 140) found values of 27.6 - 27.7 k cal/mol for hydrolysis in concentrated sulfuric acid. Daruwalla and Shet (51) obtained values of 26-28 k cal/mol for heterogenous hydrolysis over the 30-90° C range. Others have reported values of 27.8, 28-29, 33-34, 34.6 and 38.4 k cal/mol.

Vink (195) experimented with cellulose and cellulose derivatives which would dissolve in water and acid solutions to give homogeneous conditions. He observed that the degradation rate was somewhat higher in the earlier stages of reaction and noted that this has been attributed by others to weak links. His activation energies for hydroxyethyl cellulose, methyl cellulose and carboxymethyl cellulose were 31.1, 31.7 and 31.0 k cal/mol respectively which indicates that substituents have only slight effect on activation energy for hydrolysis of the glycosidic bond.

Nelson (136) says that energy of activation for hydrolysis is temperature-sensitive and increases about 65 cal/mol/deg. in the temperature range 80° - 200° C, but apparent activation energy is not much different for readily accessible and difficultly accessible regions.

According to Wessel (197) many chemical reactions which proceed with reasonably slow rates at room temperature require about 25 k cal/mol for activation. This means that the similarity between energy of activation for hydrolysis and those values determined for loss of physical properties cannot be taken by itself to indicate that hydrolysis is the only reaction occurring in deteriorating paper.

Oxidation

Oxidation reactions are thought to contribute to paper deterioration but our understanding of them is not good. Parks and Hebert (147) noted that ageing is faster in air than in nitrogen. Major (128) saw that in all cases degradation is faster in oxygen atmosphere with oxygen acting as a non-specific oxidant. Cellulose is oxidized by air in very alkaline media as discussed by Golova et al (73, 74). Ludanov and Shishkina (122) calculated an activation energy of 14 k cal/mol for the oxidation of mercerized dissolving kraft pulp in alkaline medium. Robert and Viallet (162) noted that the presence of magnesium salts inhibited the degradation of polysaccharides by oxygen in alkali solutions. One wonders if magnesium carbonate in paper affords some protection against oxidative damage.

Alkaline Degradation

In addition to oxidation, alkalinity, in high concentration and at high temperatures, may promote erosion and scission of the cellulose polymer chain. Though these reactions are of importance in the cooking and refining of wood pulp, it is generally assumed that they do not occur under normal paper ageing conditions . Probably few if any papers of current manufacture are excessively alkaline.

The erosion or "unzipping" reaction progressively shortens the cellulose chain by removing one glucose unit at a time. Attack occurs at a reducing end group and removes a single unit, leaving a new reducing end group. This continues until a slower, competing "stabilization" reaction produces a non-reducible end group on that chain (27).

Alkaline scission of cellulose cuts the polymer chain into shorter sections, thereby reducing the degree of polymerization. Carbonyl groups along the chain of oxidized cellulose are very vulnerable to alkali. It has been reported that scission will occur at nearly all such groups in one hour at room temperature in 0.05 N sodium hydroxide (27). The possibility that this might occur in paper deserves investigation

and there is a need to know at what level alkalinity becomes harmful to paper.

Crosslinking

Back and his co-workers (8, 11, 9, 10) have suggested that crosslinking which occurs in ageing paper has been too much overlooked. A wet breaking length of 40-50% of the dry value can be developed in two weeks at 70° C or 2 minutes at 200° C. The crosslinking which produces this also causes an increased stiffness which lowers folding endurance. The increased bonding would also be expected to lower tear resistance.

It has been shown that folding endurance and tear resistance generally decline more rapidly in acid papers without regard to their other characteristics, especially under moist ageing, and that the energy of activation for the loss of these properties is about 25-30 k cal/mol (37, 134). Evidence such as this has strengthened the assumption that hydrolysis is the major degrading reaction but Back (8) reports crosslinking is also catalyzed by acidity and that its activation energy is 20-30 k cal/mol.

Hechler (79) observed an increase in wet strength of laboratory sheets heat treated above 80° C. The increase depended upon temperature, time of treatment, type and condition of fiber.

Wilson et al (201) have said that changes in fatigue properties may be due to relaxation of secondary valence forces or increased crystallinity. Crosslinking is also a possible explanation.

Higgins (83) showed that mild oxidation decreases tensile strength but that higher degrees of oxidation produce permanent increases in tensile and brittleness while reducing extensibility and folding endurance. IR analysis of periodate-oxidized cellulose shows the increasing presence of carboxyl groups with increased oxidation. The heat of formation for carboxyl groups in heat treated cellulose is reported (170) to be 6 k cal/mol.

Back (8) showed that pre-oxidation of pulp with periodate increased the velocity of crosslinking but that pre-reduction with sodium borohydride lowered the rate of crosslinking. This suggests that a reducing pre-treatment for pulp might improve the service life of paper by reducing the number of oxidized sites available for crosslinking.

Back and Klinga (9, 10) observed that crosslinking reactions take place at very low relative humidities when paper and fiber are at their smallest dimensions. On reconditioning the crosslinked bonds oppose the re-expansion of the samples to their original dimensions. This change in hygroexpansivity offers one way of measuring degree of crosslinking.

If crosslinking can also occur under more moist conditions and at temperatures lower than the 70° C minimum Back worked with, it may be a significant part of natural ageing. If this is not the case, accelerated ageing in dry ovens will be unlike natural ageing in this respect. Further, if crosslinking does not occur in moist ageing, none of the greater rate of deterioration observed for moist ageing would be attributable to it.

Graminski (76) observed increases in extensional stiffness as a result of ageing at 90° C, 50% relative humidity. He attributed this to crosslinking or an increase in the degree of crystallinity.

Parks and Hebert (147) noted increased wet strength as a result of dry ageing of pulps which had been deashed with hydrochloric acid and pulps treated with aluminum sulfate. This was not observed in the same pulps when they were aged under humid conditions but it was observed in untreated pulps aged under humid conditions. They surmised that crosslinks are formed under both dry and moist conditions but that in the treated pulps which develop acidity they are hydrolyzed when moisture is present.

Though Back believes crosslinks to be primarily hemiacetal, he notes that some of those formed in heat treatment are not hydrolyzable and suggests that ether linkages are also formed.

Aluminum sulfate and ferrous sulfate which may cause a high level of acidity in the paper promote rapid increase in wet strength upon heat treating at first, and then a decline. Cations having a high redox potential usually produce high maximum wet strength (8). Back believes heat and acidity promote hemiacetal crosslinking with carbonylic sites or carbonylic radicals and that a high redox potential promotes formation of the carbonylic sites.

Accelerated Ageing Conditions

There has been much discussion as to the most meaningful conditions for accelerated ageing and many ways of doing it have been proposed and used.

The oldest heat ageing methods involved the use of ovens which provided no control of moisture content in the paper. At the Barrow Laboratory all ovens are supplied with air having a 53° dew point to give a uniform absolute humidity, whatever the ageing temperature. Whether this is done or an oven is simply supplied with available ambient air, the resulting paper moisture content is quite low. This "dry" ageing has been used by many and much data from it has been published (12, 15, 18, 43, 58, 81, 134, 157, 159, 193). Its simplicity and the accumulated experience make this an attractive method.

Browning and Wink (37) suggested that if the effect of temperature is to be studied, other factors should be kept constant, especially moisture content which has been shown to affect deterioration rate. This may be accomplished by supplying accelerated ageing

ovens with air containing the proper moisture content or by ageing samples conditioned to the desired moisture content in sealed tubes. They reported identical comparisons between papers from the two methods though it might have been thought that limited oxygen supply and retention of degradation products would have caused sealed tube ageing results to be different. Sealed tube ageing was 11.6 times faster at 105° C than ageing in a dry ventilated oven.

There is not agreement as to whether sealed-tube ageing is more or less like natural ageing.

Yabrova (150) and Parks and Hebert (147) and many others report that moist ageing is faster than dry ageing. Luner (124) believes moist ageing is more like natural ageing but says that the ageing acceleration due to moisture varies greatly. Its presence leads to hydrolysis of glucosidic linkages in cellulose and hemicellulose and probably accelerates reactions of trace metals and extractives with cellulose.

Wilson and Hebert (204) aged 19 commercial papers at 90° C and 50% RH as was suggested by Browning and Wink (37). Their apparatus consisted of glass vessels immersed in an oil bath at the desired temperature and supplied constantly with air which had been bubbled through water at 72.8° C. Fifty percent relative humidity produces a much lower moisture content in paper at 90° C than at normal temperature but moisture content under these conditions would be more nearly "natural" than in a ventilated oven. Their arrangement offers the advantages of relatively uncomplicated humidity control and simultaneous ageing of several samples without cross-contamination.

Luner (124) and Cardwell (40)suggest that the effect of temperature and moisture content cycling which are a part of natural ageing, and inevitably have their effect upon paper structure, might profitably be considered in the planning of accelerated ageing research. Cycling results in more rapid ageing whether in ovens or sealed tubes.

Wilson et al (201) mention a set of papers stored in an air conditioned building for 15 years which showed very little loss of folding endurance. The moisture content fluctuations which attend normal ageing may be partly responsible for the fold losses usually observed. This should probably be taken into account in the storing of samples for non-accelerated ageing.

Cardwell (40) and Luner (124) recommend that ageing temperature should be between 60 and 120° C and normal (3-8%) moisture content should be retained by the samples. Temperatures below 60° C are too slow and pyrolysis begins at very high temperatures.

Since the purpose of accelerated ageing is to duplicate natural ageing, the degree to which this is accomplished is the proper measure of a test method's validity. It seems logical that moist ageing which maintains a more nearly normal moisture content in the paper might do this better than dry oven ageing but this has not yet been well demonstrated. Until it is, moist ageing, even though faster, will probably not completely replace the more convenient dry ageing method.

There is a real need for long-term natural ageing data which includes both chemical and physical tests run on a variety of papers at regular intervals over many years. This would increase our knowledge of the ageing phenomenon and facilitate selection of the most meaningful accelerated ageing method. The benefits from such a program will not come immediately but the long-range value of it would be great.

Physical Testing

Several physical tests have been used as indicators of deterioration in the ageing of paper. Some are more affected by ageing than others. Cardwell (40) listed the following tests in order of decreasing sensitivity to ageing: 1) fold, 2) tear, 3) breaking length, 4) burst, 5) breaking load, 6) elastic modulus and 7) brightness.

Rasch, Scribner, Wilson et al (159, 166, 201), who have compared natural ageing up to 26 years with accelerated ageing for 72 hours at 100° C showed "fair correlation between natural and artificial ageing." They observed that folding endurance was sensitive to both types of ageing but that tensile strength was little affected by either.

Mehra (132) says that folding endurance drops considerably in old and aged papers but tensile strength does not change appreciably. Spirova and Flyate (178) and Belenkaya et al (23) agree that breaking length is less affected by ageing than folding endurance. Skidmore (171) found that liner boards and corrugating media which had aged naturally for 24 years lost very little of their tensile strength. McKee (131), however, reported that, though tensile strength was less affected by oven ageing than other physical tests, naturally aged papers have low tensile values.

In some cases a heat-aged paper may lose half of its folding endurance before a significant loss in tensile strength occurs (123). This suggests that the folding endurance loss may be attributed largely to embrittlement rather than loss of strength. Zero-span tensile declines upon ageing more rapidly than 4 inch span tensile (33). This may be because crosslinking partially makes up for loss of fiber strength in finite-span testing. Cardwell (40) has concluded from his accelerated ageing of pulps that loss of strength results from a slow loss of fiber strength and a "marked increase in inter-and intra-fiber bonding."

Luner (124) says tensile failure may begin with failure of a fiber or an interfiber bond but that probably few complete failures occur with interfiber bond failure only. Bonded area, as measured by scattering coefficient, does not vary significantly during ageing. Loss in tensile strength would suggest that bond strength has decreased but it is known that when paper is heated, wet strength may increase greatly (9, 10, 8).

Though the bond strength of paper is probably increased by heat ageing, the tensile value declines and it is suggested that the brittleness which results from crosslinking reactions is responsible.

It has been pointed out by Barrow (17) that machine direction folding endurance may deteriorate faster than cross direction folding endurance but, because of its (usually) greater initial value the two reach low values simultaneously.

A convenient and dependable fatigue test which relates well to use conditions is needed for permanence testing. MIT fold testing, as it is now practiced, does not quite fill this need. It can be time-consuming and data from it is very disperse because of the inhomogeneity of paper itself and the many factors which affect its result.

Cardwell et al (41) have proposed a method based on a linear relation between log of the tension and the folding endurance value. This would permit one to estimate the folding endurance for a given tension from that at other tensions. If the chosen tension value is always a standard percentage of the breaking strength, then comparisons of two different papers may be made more meaningful by reducing the effect of breaking strength upon the final result. This method would offer a time saving because it would permit stronger unaged samples to be tested at higher tension than aged ones without jeopardizing the comparability of the data. Though the constants in the log tension vs fold relation are not the same for all papers, he reports that they do not change for an individual paper as it ages.

A possible alternative use of the relation between tension and fold would be to report folding endurance in terms of the tension required to give a fixed standard number of folds (e.g. 300) before failure (41).

If further experience confirms the log tension-fold relation, it will be much more meaningful than the statement now included in the TAPPI method (T-511) for MIT fold. It says "The number of folds may vary by as much as the cube of the applied tension." Much greater differences between .5 kg testing and 1.0 kg testing have been observed at the Barrow laboratory (Part VIII, b, this report) than would have been predicted by the TAPPI statement. Dixson and Nelson (58) tested papers at both 1.0 kg and 0.5 kg tension and calculated correlation coefficients for the two types of data of 0.95 or better in ten of thirteen cases and no coefficient was lower than 0.89.

Cardwell (41) discussed the effect of several physical aspects of the MIT folding endurance test and made the following recommendations to minimize their influence.

a) Dead weight setting of tension.

b) Good lubrication of the plunger and placing the weight in such a way as to reduce the effect of plunger friction.

c) Placing the samples in a vertical position so that the line of fold is perpendicular to the edge of the sample.

d) Always placing the samples with the felt side against the same (fixed) jaw.

e) Always making the first fold in the same direction.

f) Avoidance or removal of heat buildup on the fold line.

g) Relative humidity control at least as good as the 50 ± 2% prescribed by TAPPI (183).

At the Barrow laboratory the MIT spring scale is calibrated with a weight and sample tension is carefully set by the spring scale in the belief that it can be done more reproducibly this way because there is less effect from plunger friction.

Kahlson and his coworkers (102, 103) have discussed the effect on folding endurance of heating at the fold line and proposed means of reducing it. The use of a blower which became part of the TAPPI MIT folding endurance test method, T-511 (186) in 1969 was intended to prevent a heat buildup in the folding head and along the fold line.

The Elmendorf tear tester is commonly used in permanence/durability evaluation. Its results are not nearly as sensitive to ageing as folding endurance but it measures a property which is important to the durability of book papers. The manner in which this instrument tears a specimen is more comparable to the way in which pages are torn in the normal use of a book than any other test presently available. It has been noted that Elmendorf tear results are not as comparable to other measures of physical strength, such as tensile, as are the results of in-plane tear testing (192). The two tests do not measure the same thing, and it is for this reason that in-plane tear testing is not recommended. Book papers need resistance to the Elmendorf type of tearing.

Air Conditions for Physical Testing

Humidity and temperature affect the physical properties of paper. Crook and Bennett (48) have developed extensive data demonstrating the relation between these factors and a variety of physical tests. They have shown that meaningful comparisons of physical test data demand good control of air conditions. If practical, a higher degree of relative humidity control than the ± 2% required by TAPPI (183) would be desirable.

Wink (209) has said that variations of temperature and humidity within the TAPPI-prescribed testing conditions may cause variability of a few percent in physical test results but that, except for folding endurance, only small improvements in the variability of results would be achieved if the tolerances were halved. Such control is not

easily achieved and he believes more can be accomplished at less expense by the prevention of hysteresis effects and due attention to moisture content history and stress relaxation which results from fluctuation of moisture content. Relative humidity excursions above 65% are particularly to be avoided.

Moisture hysteresis effects are several times greater than the effects of temperature and humidity, but they can be essentially eliminated by always approaching equilibrium with the testing atmosphere from a drier (less humid) atmosphere(209). When physical test results on unaged samples are to be compared with data from samples which have been heat-aged in a dry oven, the unaged samples should be well desiccated before being conditioned for testing.

Comparisons of Longevity

Barrow, in his tentative specifications of 1958 (43), proposed a minimum acceptable initial strength and minimum acceptable deterioration rate. In a later publication (17) he categorized levels of paper strength and defined a level of unusability. This was useful in predictions of useful life, and in arriving at desirable relative values of initial folding endurance and tear resistance. Browning (36) also mentions the need of defining a "critical level" of paper properties. It has been pointed out that a paper's rate of deterioration may be slightly higher than the prescribed minimum but if its initial strength is well above the prescribed minimum it may actually reach unusability at a point later in time than a paper which barely meets both minima. Since the objective of such specifications is to assure maximum longevity, this possibility should be taken into account in the writing of new specifications.

Chemical and Physical Properties

Fink and Zwicky (64) examined old papers and papers about ten years old and

subjected newly made papers to accelerated ageing (100° C, 3 days). They concluded that the old papers had undergone some ageing, the 10 year old papers showed no significant signs of ageing and the heat aged new papers showed slight ageing, but that all were still perfectly suited to performing as book papers. This is quite believable but it does not prove a high degree of permanence for either the new or 10 year old papers. They question the importance of folding endurance as an indicator of ageing, saying that almost no cellulose decomposition may occur when there is a folding endurance loss. However, if one evaluates paper in terms of properties which relate to its use it is difficult to choose a test more meaningful than folding endurance.

Yet chemical tests do have their uses and they will become more useful when their results can be better related to physical properties and degree of degradation. The pH test, for the effort involved, is the best single measure of a paper's probable permanence.

Millett and co-workers (134) found straight-line relationships when the log percentage of initial value was plotted against ageing time for fold, tear and tensile, but when the log residual degree of polymerization was plotted against heating time the lines were curved (133).

The connection between yellowing and loss of strength has not been well established (204). The relations between functional groups and mechanical properties of aged papers are not clear but it appears that mechanical properties, though adversely affected by oxidized groups, do not follow the relations established between color reversion and functional groups (124).

Chemical Tests

Several chemical tests have been used to characterize pulps and papers and measure their deterioration.

Gluchowska and Winczakiewicz (71) found good correlation between the chemical properties of naturally aged (1 and 6 years) and artificially aged (100° C 72 hours) papers but had little success with physical properties.

McKee (131) observed that upon heat ageing, folding endurance and alpha content dropped similarly and the copper number increase was correlatable with the alpha content decline.

Alekseeva (2, 1) found that rosin sizing caused a substantial increase in copper number of kraft, cotton and flax when they were heat aged but that the presence of fillers (calcium carbonate or kaolin) largely prevented this. There was good correlation between carbonyl content and yellowing.

Rasch, Scribner, Wilson et al (159, 166, 201) showed good correlation between chemical properties and stability. Their chemical tests were for alpha content, copper number and acidity.

Flyate and Afonchikov (65, p.1) say that the yellowing from heat and ultraviolet radiation is usually accompanied by a decrease in viscosity and degree of polymerization, and increases in copper number and sodium hydroxide solubility.

Iuchum (97) suggested the measurement of cellulose degradation by tests for dichromate number and alkali solubility. Yabrova (150) says alkali solubility is the test most indicative of the ageing process. Belaya (24) measured the content of substances soluble in 7.4% sodium hydroxide. He was able to correlate minimum strength loss and pH stability with a constant amount of alkali solubles for flax and cotton papers.

Venter (194) found degree of polymerization and 1% alkali solubility to be the most sensitive chemical indicators of ageing and says that they are more sensitive to ageing than strength properties. Winczakiewicz (206) chose average DP and cross direction tear as the best indicators for ageing of insulation papers.

Pravilova and Istrubtsina (65, p. 72) observed pH decreases of the order of 0.5 unit for commercial and printing papers aged 3 days at 100° C, and Parks and Hebert (147) were able to correlate acidity increase with loss of fiber strength.

Illukowicz (94) thought that pH values determined by cold extraction were more meaningful than those determined by hot extraction. Pravilova (153) compared hot and cold extraction and concluded that cold extraction merited recognition as a standard test method. Barrow (14) used both methods on heat-aged papers and found that cold extraction results correlated better with paper deterioration.

The use of flatheaded electrodes for measuring the pH of a paper at its surface offers the advantages of speed and non-destructive testing. Illukowicz's "contact method" (94) gave results which compared well with extraction methods. Hudson and Milner (91) obtained results which agreed closely with the cold extraction method. Flynn and Smith (68) did not find good correlation with the cold extraction method. Ray (160) found good correlation between hot extraction and surface results on book papers but not on other types. He reported that the U. S. Government Printing Office has adopted the flathead technique as a screening test. The use of a single probe combination electrode has been studied at the Barrow laboratory and is presently being considered by TAPPI as a suggested method under Committee Assignment 8617.

Palenius et al (145) have investigated the realiability of different pH measuring procedures and found that variations are most often due to the water used, airborne impurities, condition of equipment and standards of cleanliness.

Langwell (117) proposed the use of bromcresol green indicator applied from a pen as a means of evaluating the approximate stability of a paper. This indicator changes color over the pH range 3.6 to 5.2. Since even the upper end of this range is undesirably acid it would appear that this is not the best indicator for separating stable and unstable papers. Chlorophenol red (21) or another indicator which changes color closer to neutrality would be a better choice. The use of ball point pens or felt-tip markers appears to be a very convenient and practical method of application. King, Pelikan and Falconer (107) on the basis of 17 comparisons concluded that the Archivists' Pen or a calibrated universal pH indicator gave reasonable estimates of surface pH but noted that surface pH may not be representative of the whole sheet.

Thermal Analysis

The idea of using a rapid method like thermal analysis for permanence evaluation is certainly attractive. Such a test would require only a fraction of the time consumed in heat-ageing and testing of paper samples. The applicability of thermal analysis to this problem has not yet been established but work is being done in this area and it shows some promise.

Hebert, Tryon and Wilson (78, 202) tested a variety of papers using thermal analysis. They observed two endothermic peaks due to loss of sorbed moisture and to massive decomposition. The temperature of the decomposition endotherm correlated well with pH values - the more acid papers having decomposition endotherms at lower temperatures.

Parks and Hebert (148) have shown that deashing lowers the temperature of the decomposition endotherm but not as much as the presence of aluminum ions. Calcium ions retarded volatilization and shifted the decomposition endotherm toward higher temperatures. Parks also observed this in oxidized celluloses (146). Both the aluminum ion and the sulfate ion of aluminum sulfate apparently contributed to a shift of the decomposition endotherm toward lower temperatures.

Arseneau (6) has studied cellulose degradation in the 150° - 400° C range and discussed the nature of the reactions involved. Though they are different from those assumed for the usual accelerated ageing and normal ageing temperature, it may be possible that the behaviour of paper at such high temperatures may be related to its permanence.

Cardwell (40) did not find good correlation between thermal stability as measured by activation energy and the deterioration of heat-aged papers. This was taken to mean that the rate-determining step at pyrolysis temperatures is not the same as that for the lower accelerated ageing temperatures. He did find a relation between features of a paper's thermogram and its accelerated ageing rate which might be adequate for coarse screening of pulps for permanence characteristics.

Conrad et al (47) using fluidity measurements, reported an energy of activation for thermal chain cleavage in cotton of 25.2 k cal/mol. Arthur and Hinojosa (7) using electron spin resonance derived an activation energy for thermal initiation of free radicals and chain cleavage of about 33 k cal/mol. which is well within the range of values reported for acid hydrolysis.

Fung (69) reported first order kinetics with an overall activation energy of 35.4 k cal/mol. for pyrolysis of cellulose in vacuum at 200-280° C. Degradation in air (83) at 250° C showed oxidation initially in the formation of carbonyl groups, and the reaction penetrated crystalline regions, as evidenced by disappearance of the carbohydrate spectrum.

Ivanov et al (101), held that the thermal stability of the pyranose ring is quite good but that cellulose is more vulnerable at acetal bonds, open ring units such as those in which carbons 2 and 3 are oxidized to aldehydes, and units in which the hemiacetal bond is broken. They demonstrated that these situations could be stabilized with para-phenylenediamine.

Because the reactions of pyrolysis and heat ageing are different, it is unlikely that thermal analysis will completely supplant accelerated ageing and physical testing of samples but its possibilities should be thoroughly explored.

Recommendations for Future Research

It now appears that further research in the following areas would add significantly to knowledge about ageing and lead to more meaningful test methods as well as longer-lasting papers.

1) The relative comparability of moist and dry ageing with natural ageing.

2) Standardization of accelerated ageing methods and criteria for measuring deterioration.

3) The relative contributions of hydrolysis, oxidation, crosslinking and other reactions to apparent physical deterioration.

4) The reactions which determine overall activation energy for paper deterioration.

5) The need for a fast, meaningful fatigue test.

6) The possibility that an economically feasible pre-reduction treatment might reduce the embrittlement rate of papers.

7) The possibility that radical scavengers, antioxidants and complexing agents might be used to prolong the service life of paper.

8) Thermal analysis as a means of measuring normal-temperature stability.

9) Determination of the level at which alkalinity becomes harmful to paper.

10) A very long term natural ageing program with carefully controlled periodic tests. A paper archive.

Recommendations for Permanence/Durability Evaluation

1) Temperatures between 60° C and 125° C are recommended for accelerated ageing.

2) Accelerated ageing temperatures should be controlled precisely.

3) Ovens should have forced air circulation.

4) Dry oven ageing is currently recommended.

5) Deterioration rate is more accurately determined from ageing schedules which include several heat-aged points.

6) Folding endurance is recommended as the most sensitive physical indicator of deterioration.

7) The folding endurance test should be run in strict accordance to the prescribed method. All samples should be put into the machine in the same way and the first fold should always be in the same direction. Because of the dispersion of fold data, a minimum of 25 tests of a kind are recommended for meaningful averages.

8) The Elmendorf tear test measures a property which is very important to durability.

9) When physical test results are to be compared, all samples should approach equilibrium with the test air conditions from a drier condition.

10) Estimation of service life requires an objective definition of the point at which a paper becomes unusable.

11) The pH test is the best single simple indicator of probable permanence. The cold extraction method is recommended.

IV. Current Commercial Papers

The setting of specifications requires not only a knowledge of what is desirable but also a knowledge of what is possible or available. The testing of commercial papers which are offered as long life papers fills this need.

Thirty-two papers were examined. They were obtained by soliciting manufacturers directly and through an invitation which appeared in two journals. Throughout this report these papers will be identified by number only in order to preserve the manufacturers' anonymity.

Table 1 gives some of the characteristics of these papers. pH values were determined by cold extraction, rosin content by the Raspail (TAPPI method T-408) test and carbonate content by immersing pre-wetted samples in ca. 3% HCl. With the possible exception of Paper #128, none contained groundwood. The fiber content, where given, was provided by the manufacturer.

Each of these papers was tested for folding endurance and tear resistance in machine and cross directions, both as received and at 6 day intervals during a 30 day period of ageing at 100° C in forced circulation ovens supplied with air having a 53° F dew point. Cold extraction pH determinations were also made for each ageing interval.

The results of these tests are shown in Table 2 and lines were fitted to the data on semi-log coordinates by the least squares regression formulae. An example appears at the end of this report (Fig. 5). Each folding endurance value is the mean of 50 tests run at 1 kg tension on the same MIT instruments. Each tear resistance value is the mean from ten 8-ply tests. All physical tests were run at 73 ± 1° F and 50 ± 2% R.H.

If a paper is to have a long service life it must be strong (durable) when it is new and must deteriorate slowly (permanence). Table 3 summarizes these properties for the papers tested. Initial C. D. fold and M. D. tear, being the weaker directions of these most important strength properties, have been used as durability criteria for ranking these papers. The criterion chosen for permanence ranking was percent retention of M. D. folding endurance after 24 days of ageing as calculated from the least squares deterioration line. M. D. fold has been shown to be the physical property most sensitive to heat ageing.

There are great differences in the paper properties. Papers which may be very good in some respects are mediocre in others and the relative permanence/durability of different papers is not obvious. An attempt has been made to rank the twenty 60 pound (including 57 and 63 lb.) papers using the criteria of M. D. fold retention, initial C. D. folding endurance and initial M. D. tear resistance. Each paper's ranks from Table 3 on these three tests were simply added together and the sum used as an indicator for comparing lasting qualities. These may be seen in Table 4.

Paper #125, an all-cotton paper is in second place in overall permanence/durability among the 60 lb. papers (Table 4) largely because of its high initial strength. No other paper of similar weight showed higher folding endurance or tear resistance (Table 3). It is interesting however to note that two chemical wood papers had higher folding endurance and that one of them was lighter (45 lb.) and the other heavier (80 lb.). The heavier one, Paper #112, was made very strong for use as end leaf. The lighter one, Paper #132, was one of five 40-45 lb. papers tested, all of which were among the twelve having highest folding endurance.

Though the lighter papers are not included in the comparisons of Table 4 it should be noted that Papers #101, 102, 103, 106 and 132 had folding endurance greater than 30, tear resistance greater than the numerical value of their basis weight and over 50% M. D. fold retention after 24 days of ageing.

It was surprising that Paper #128 which was made entirely from uncleaned, reclaimed, chemical wood fiber placed eighth among the 60 lb. papers in overall permanence/durability (Table 4). It may not have good color stability.

Durability has been measured in terms of initial C. D. fold and M. D. tear. Permanence may be measured in terms of M. D. fold retention alone. Table 5 shows that M. D. tear, which is an entirely different physical test and produces failure at 90° to the M. D. fold line of failure, ranks the 32 papers tested very similarly. Eight of the ten papers having highest M. D. fold retention were among the ten papers having highest M. D. tear retention.

Tear testing can be done much more rapidly than fold testing, but because of its relative insensitivity to heat ageing, it is not recommended for permanence evaluation. If it were to be used, 85% retention of initial M. D. tear after 24 days of ageing at 100° C would indicate a high level of permanence.

It is apparent from Table 3 that there are several permanent papers available today. Unfortunately, not all of them have the strength to merit the "durable" designation as well.

V. Effect of Relative Humidity in Accelerated Ageing

Accelerated ageing in ventilated ovens dries the papers to a much lower moisture content than that which would be observed under normal ageing conditions. It has been suggested that accelerated ageing would be more like natural ageing if it were done in a more humid atmosphere and several investigators have reported that deterioration is more rapid in papers that are not dry. This refers to the deterioration of paper itself and not the very destructive effects of mold and mildew which thrive in excessively moist conditions.

Rates of folding endurance and tear resistance loss have been determined for two papers at 76° C and four different relative humidities. The humidities used were 20, 35, 50 and 65% RH.

The two papers were #115 and #116. Their mean initial C. D. fold values were 51 and 11, respectively and initial M. D. tear resistance values were 73.5 and 56.1. Both are neutrally sized, slightly alkaline, and contain calcium carbonate filler.

Before ageing was begun enough matched samples of fold and tear specimens were prepared so that all ageing could be done on comparable groups of specimens. Since ageing at all four humidities could not be done simultaneously a new set of unaged control samples was tested at the beginning of each ageing schedule. Samples awaiting ageing were stored in the ream of paper from which they were taken.

Ageing was done in a Blue M Vapor-Temp apparatus. The chamber of this device is a large glass dome which permits access of light to the contents. Sample sets were removed from the chamber for testing at intervals of 18 days up to a total of 90 days at each humidity. Those aged at 50% and 65% RH were desiccated over calcium chloride before being conditioned for testing. At each ageing interval 50 individual MIT fold

tests (1.0 kg tension) and ten 8-ply Elmendorf tear tests were run. Cold extraction pH was determined on scraps from the tear test. Samples were accumulated until the end of each ageing schedule so that pH tests on them could be run simultaneously.

Tables 6 and 7 contain the results of these tests. This data was plotted on semi-log coordinates and the least squares linear regression method used to fit a line describing deterioration. Percentage retention of original strength was calculated from each of these lines and is shown in Table 8. This shows that in all eight cases deterioration was more rapid at 65% than at 20% but there are too many inconsistencies in the data for the intermediate humidities to permit a quantitative general statement about the relation between relative humidity and deterioration rate. A useful extension of this work would be the ageing of the same papers at the same temperature without any humidification of the air.

It will be noted in Tables 6 and 7 that pH generally changes very little during the ageing schedule for one humidity. This is taken by some to be an indication of good stability. Since all the pH tests for one humidity were made at the same time, these comparisons are particularly meaningful. However, it will also be noted that the pH values for different humidities, even on unaged control samples, are variable.

The effect of relative humidity on ageing rate needs more study. Though dry oven ageing is more convenient, moist oven ageing is faster and if it can be shown that it also produces results chemically and physically more like those of natural ageing, moist ageing should be used in permanence evaluation. For the present however, dry oven ageing adequately fills the need for an accelerated ageing method.

VI. Effect of Basis Weight on Folding Endurance and Tear Resistance

Strength and thickness of a paper depend to a significant extent upon its weight. In this project 60 lb. papers were tested where they were available. In order to facilitate comparison of papers of different weights this effort was made to develop a general idea of how folding endurance, tear resistance and thickness vary with the weight of a paper.

Four papers in basis weights of 50, 60 and 70 pounds per ream and one paper in the 50 and 70 pound weights were tested.

For each direction of each paper 300 fold specimens of each weight were prepared. 60 of each weight were tested on each of 5 machines. For each paper small groups of each weight were tested in rotation so that there would be no differences in conditioning history and testing conditions among the different basis weights. Tear resistance testing was handled in the same way with the same instrument being used for all tests. All samples were desiccated over calcium chloride before being conditioned for testing which was done at 73° F and 50 ± 1% R. H.

Complete results are given in Table 9. Each folding endurance value is the mean of 300 individual tests and each tear resistance value is the mean of 16 eight-ply tests. Each thickness is the mean of 128 readings. Calculated basis weight was determined from the weight and exact dimensions of the sheets sampled for machine direction tear resistance.

Except for Paper #116, the data in Table 9 fits the supposition that folding endurance of a paper increases with increasing basis weight until it reaches a maximum for that paper after which increasing thickness causes a lowering of folding endurance. Tear resistance increases with basis weight, usually more than proportionally. Thickness increases with basis weight approximately proportionally. This is shown in Table 10.

It is not correct to assume when a commercial paper is offered in more than one weight that all sheets of that name are alike in all respects but weight. Differences in loading are common. Differences in fiber preparation and many other variables in the papermaking process may affect the nature of various weights. Factors of this sort may explain the anomalous fold data reported for Paper #116 in Table 9 and probably influenced to varying and unknown degrees the other results given there.

It appears then that if the tear resistance and thickness of a paper are known for one basis weight, they can be roughly estimated for another similar weight, but that this should not be attempted for folding endurance.

VII. Effect of Variables in the MIT Folding Endurance Test

The folding endurance test is one of the physical tests most sensitive to paper deterioration. Because of this and the fact that the ability to endure folding is an important property in book paper, this test is very useful in studying permanence and durability. There are several ways in which the MIT folding endurance tester may be used and the purpose here is to evaluate the effect of some of these variations upon the results.

These five variables were studied:

a) Spring loading as compared with dead weight loading.

b) 1.0 kg tension as compared with 0.5 kg tension.

c) Fan-cooled as compared with uncooled tester jaws.

d) The direction of the first fold.

e) Variation in radius of curvature of folding edges.

The first four questions were examined by testing the machine direction folding endurance of five different 60 lb. papers in all of the ways necessary for the desired comparisons. Before testing was begun, eight matched sets of 100 fold specimens were prepared from each paper. All testing was done on the same machine with modifications being made as required. All samples were desiccated before conditioning for testing and all testing was done at 73 ± 1° F, 50% ± 1% R. H.

The means for all these tests are shown in Table 11 and they are discussed below.

a) Spring Loading vs Dead Weight Loading

It has been assumed here that a dead weight will apply tension more uniformly and reproducibly to fold specimens than the short spring scale which is commonly used for paper testing. A machine was converted to dead weight loading and an attempt was made

to evaluate the difference in the two modes of testing to learn whether or not they give significantly different results and if the spring scale gives more disperse results.

The means and measures of dispersion for the five papers tested are shown in Table 12. Each mean represents 100 individual tests. It will be seen that when data obtained with spring tension is compared with data obtained with dead weight tension the two standard deviations tend to differ as the means for the two types of data differ. More meaningful comparisons may be made with coefficients of variation. This is a relative measure of dispersion obtained by dividing the mean into the standard deviation.

Coefficients of variation given in Table 12 show that relative dispersion for spring scale testing and dead weight testing are very similar. It is then concluded that the dead weight offers no advantage over the spring scale in terms of reducing dispersion of data.

Though the differences are small, it is noted in passing that in all five comparisons at .5 kg tension, spring scale testing gave the higher coefficients of variation whereas at 1.0 kg tension, dead weight testing gave the higher coefficients in 4 out of 5 cases.

The means shown in Table 12 for the two types of testing are different but in some cases because of the natural dispersion of fold data there is uncertainty as to whether or not these differences are meaningful or simply due to chance. The hypothesis that each pair of means was equal was tested at the 0.01 significance level. Results are shown below.

Comparison of M. D. Folding Endurance
with Spring Scale and Dead Weight

	1 kg tension			.5 kg tension		
Paper	Spring Scale		Dead Wt.	Spring Scale		Dead Wt.
#104	24	=	22	266	<	370
#105	183	=	173	1924	<	2309
#115	117	<	148	1508	<	2185
#116	19	<	23	332	<	407
#118	12	>	11	103	<	139

In 7 cases out of 10 the dead weight results were significantly higher. There were 3 cases in which the spring scale mean results were higher but in only one case, where the results were numerically small, was the difference significant at the .01 level. It is therefore concluded that the use of the dead weight in place of the spring can be expected to increase the folding endurance results.

The lower values obtained with the spring scale could have resulted from slight increases in tension which occur as the specimen wraps around the folding edges and pulls down against the spring scale. This does not occur in the dead weight arrangement because the weight is suspended by a light spring which absorbs this motion.

Since the use of the dead weight does affect the value of the result and does not improve precision it should not be used for paper testing while the spring scale is standard in the industry.

b) 1.0 kg Tension Compared with 0.5 kg Tension

In time past, this laboratory has done most of its folding endurance testing on book papers at .5 kg tension rather than the 1.0 kg tension which is generally used throughout the paper industry. It was thought that folding at the lower tension was more nearly like the flexing of paper which occurs in the normal use of books. The higher numerical value of the result permitted more discrimination in the comparison of aged samples. Very weak papers simply would not give a useful result when tested at the higher tension.

It was decided at the inception of this project that an updated folding endurance specification would be in terms of 1 kg tension testing. This would greatly reduce the time required for evaluation of a paper while still giving a useful measure of the paper's flexibility. Further, it was felt that truly permanent/durable papers would give a test result at the higher tension which would be numerically great enough, even after ageing,

to permit meaningful comparisons.

It is useful then to test some papers at both 1.0 and .5 kg tension in order to gain some ideas of the relation between the two test methods. The data reported in Table 1 permits this comparison to be made for five different papers under four different testing conditions.

Table 13 shows that when the tension is doubled from .5 to 1.0 kg the folding endurance for these papers is reduced by factors ranging from 8.6 to 17.7. The geometric mean of all these ratios is 12.8 but their variation is so great that it would be poor practice to use a single factor for all papers in converting results obtained at one tension to their equivalent at another tension.

TAPPI method T-511 su 69 for the MIT tester says "The number of folds may vary by as much as the cube of the applied tension." This rather nebulous statement seems to mean that if the tension is halved the folding endurance will be increased up to a maximum of eight times. None of the examples shown here exhibit so small an increase, and it is concluded that the TAPPI statement is of little value. The relation between log tension and folding endurance proposed by Cardwell (40, 41) could not be tested with data for just two tensions.

Folding endurance testing at 1.0 kg tension is much faster than at 0.5 kg tension. It produces results on durable book paper which are numerically large enough to afford the discrimination needed for permanence evaluation.

c) Fan-cooled and Uncooled Tester Jaws

The TAPPI standard method, T-511 for folding endurance was revised in 1969 to include a blower on the front of the machine which draws the conditioned air of the testing room over the specimen while it is being tested. The purpose of this is to keep the temperature and moisture content of the paper constantly in equilibrium with the prescribed air conditions.

It was thought that heat which resulted from flexing the specimen and heat which was transmitted to it from the friction within the machine itself would raise the temperature and lower the moisture content in paper and thereby lower the numerical folding endurance result. The degree to which this would be true supposedly depended upon how long it took the specimen to break and how long the machine stood idle between tests. Use of the blower was expected to overcome this problem.

In order to evaluate the effect of the blower on folding endurance results, machine direction testing was done on five papers with and without the fan, at both 1.0 and .5 kg tension. The same machine was used throughout and 100 tests of each kind were run.

The blower used is pictured in Figures 1 and 2. The Plexiglas cowl which encircles the folding head forces a much greater part of the air which is taken in by the blower to actually pass over the folding head and specimen. The air discharged by the blower is directed through a hole in the supporting table to a plenum from which it is dissipated without the inconvenience and uncertainty which could result from the side-by-side operation of several of these machines. It is believed that these two features make this unit superior to those offered commercially for the purpose.

Table 14 shows mean results of these tests and measures of dispersion. It may be seen that dispersion is similar for the two types of data, whether measured by standard deviations or the more comparable coefficients of variation. It may then be concluded that use of the blower does not increase nor decrease the scatter of folding endurance data.

As the tests were being done which did not involve the use of the fan, each interruption was recorded. Subsequent review shows that half of the time the first result after the interruption was higher than the last one before the interruption and half of the time the reverse was true.

Figure 1

Blower on MIT folding endurance tester in out-of-use position.

Figure 2

Blower in position for use

The mean folding endurance values given in Table 1 show little difference at 1 kg tension between results obtained with the blower and without it, but at .5 kg tension mean values obtained with the blower were higher. Considering the dispersion of folding endurance results, it is not certain whether or not these differences are meaningful.

A method using standard deviations was employed to test the hypothesis that each pair of means was equal at the .01 significance level. Results are shown below.

Comparison of M. D. Folding Endurance Data Obtained with and without a Fan

Paper	1 kg tension			.5 kg tension		
	With Fan		Without Fan	With Fan		Without Fan
#104	22	=	24	370	>	292
#105	173	<	218	2309	>	2051
#115	148	=	145	2185	>	1666
#116	23	=	22	407	=	371
#118	11	=	11	139	>	126

In 4 of 5 cases for the data obtained at .5 kg tension, the value obtained with a fan was significantly higher. In the fifth case (#116) the difference was not significant. It appears then that the fan may be expected to increase fold results run at .5 kg tension. In these comparisons the increases (in the order of the table) are 27, 13, 31, 10 and 10 percent and their mean is 18%.

No such conclusions can be drawn for the data obtained at 1 kg tension. In 4 cases there is essentially no difference. In the fifth case the difference is significant but the reverse of what was expected. No explanation is offered. If more of these comparisons were to be made at 1.0 kg tension they should be made upon papers which will have numerically high folding endurance results at that tension. It is likely that data can be developed which will show at all tension levels that use of the blower will increase the result.

Though no reduction was observed in the scatter of folding endurance data as a result of using a blower, it does tend to increase the results at least at the lower tension. The rationale for its use is sensible. Further, since it is now part of the industry standard, its use is to be recommended for the sake of comparability.

d) Direction of the First Fold

It has been suggested that the direction in which the specimen is first folded in the MIT tester will affect the total number of folds to failure. We are not aware of any published work on the subject. This possibility has been investigated by testing matched sample sets of five different papers. One hundred tests were run on each paper in which the first fold was toward the felt side and the same number was run with the first fold toward the wire side. The same machine was used for all tests. Table 15 shows test result means and measures of data dispersion.

Because of the dispersion of folding endurance results it is often not possible to judge whether two means are significantly different. A method based on standard deviations was used to test the hypothesis that each pair of means was equal at the .01 significance level. Results are shown below.

Paper	First fold to:	1 kg tension		.5 kg tension	
		Felt side	Wire side	Felt side	Wire side
#104		22 =	24	370 >	311
#105		173 <	202	2309 =	2192
#115		148 =	135	2185 >	1650
#116		23 =	24	407 >	355
#118		11 =	11	139 =	132

This table shows that at .5 kg tension the folding endurance result in 3 cases out of 5 was higher when the first fold was toward the wire side and in the other two cases the difference was not significant. At 1 kg tension there is no significant difference in four cases and in the fifth case a higher result was obtained when the first fold was toward the wire side, the reverse of what was generally noted at .5 kg tension. No general conclusion can be drawn but it does appear that at the lower tension higher results may be

expected when the first fold is toward the felt side.

This sort of question cannot be conclusively resolved without a great deal of testing. The effect of the first fold direction would be different in magnitude for each paper. Rather than try to evaluate it, it would be much more sensible to simply specify one direction or the other in the standard test method.

e) Variation in Folding Edge Radius of Curvature

It is specified (TAPPI method T-511) that the edges of the MIT folding head around which the specimen is folded during testing should have a radius of curvature of .015 ± .001". It has been supposed that if these edges are sharper than that, the folding endurance result will be lower and that larger radii of curvature will produce higher results. Since it has been noted that folding heads in use and even new ones may not meet this specification, it is useful to know to what extent test results may be influenced by deviations from the specification. There is also some question as to whether the allowable deviation of ±.001" is undesirably large.

Folding heads having edges of .012", .015" and .018" radii of curvature were made by a local machine shop to a tolerance of ±.0002". Matched sample sets of five papers were tested in both directions using the outsize heads and a standard folding head on the same machine. Fifty tests of each kind were run. Results are given in Table 16 which shows clearly and consistently that radius of curvature does affect folding endurance results, the sharper edges producing the lower results.

Table 17 which expresses the results from the outsize heads as percentages of those obtained with standard heads shows that radii of curvature lower than standard affect M. D. results more than C. D. and that higher radii affect C. D. results (with one exception) more than M. D. This is also reflected in Figure 3 which shows composite lines for the 5 papers tested.

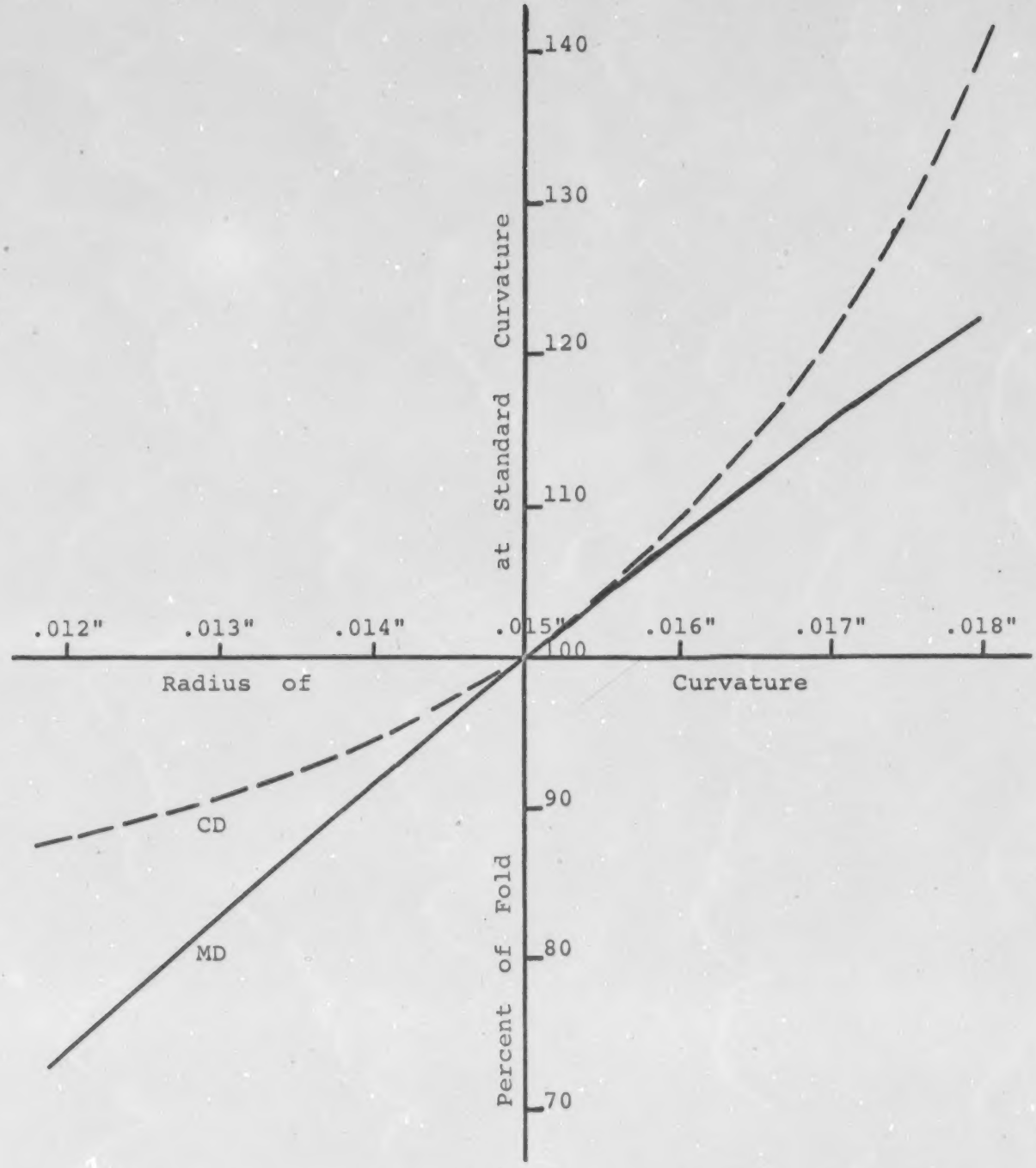

Figure 3 - Effect of Folding Edge Radius of Curvature on Folding Endurance Result

Figure 3 also suggests that when the extreme acceptable values for radii of curvature are used one may expect, on average, deviations of 8%, M. D. and 6%, C. D. for radius .014" and 8%, M. D. and 9%, C. D. for radius .016". These could be approximately halved if the tolerances on radius of curvature were halved so that the TAPPI specification would read ".015 ± .0005." " The folding endurance test produces rather variable results. This is a relatively simple way to somewhat reduce variation between machines.

Conclusions

a) Spring tension is preferred to dead weight tension.
b) 1.0 kg tension is practical for fold testing of durable papers.
c) Use of the blower is recommended.
d) The first fold should always be made in the same direction.
e) Radius of curvature tolerances for MIT folding edges should be halved.

VIII. Specifications for Uncoated Permanent/Durable Book Paper

Long lasting papers must be both durable and permanent. Durability is the level of physical strength and flexibility necessary to withstand extensive use and handling. "Permanence" in the paper vocabulary, indicates a degree of chemical stability which permits only very slow deterioration. Specifications for long-life papers require measures of both.

The term "permanent/durable" should be reserved for those papers which are superior in these respects but it is hoped that the methods suggested here will find application wherever the lasting qualities of papers are evaluated.

pH

Specifications of this kind should generally be written in terms of performance rather than ingredients and methods of manufacture. However, with the evidence available it seems safe to conclude that there simply are no permanent acid papers. There is no reason why a minimum pH of 7.5 cannot be specified as long as it is made clear that this, alone, is not an infallible indicator of permanence. This one relatively simple test would permit a user to eliminate many papers from consideration before proceeding to more involved and expensive evaluation procedures.

C. D. Fold

When durability is measured in terms of folding endurance and resistance to tearing, it is appropriate that they be tested in their weaker direction.

C. D. folding endurance at 1.0 kg tension as high as 150 is possible in 60 pound papers but lower values are much more common (Tables 3, 18). A value of 30 indicates good durability and is quite attainable for any normal book weight. Seven of the ten papers shown in Table 20 having basis weights below 60 lb. and both of these having basis weights above the 60 lb. range have folding endurance greater than 30.

M. D. Tear

70 gm is a desirable and possible level of M. D. tear resistance for 60 lb. papers (Tables 3, 19). Heavier papers may be reasonably expected to have proportionally greater tear resistance but at 40 lb. basis weight an acceptable minimum higher than 40 gm is impractical (Table 20). Such tear resistance values as these can be obtained in papers having folding endurance of 30.

Strength Retention

A general permanence specification may be set for all basis weights since permanence is expressed in terms of percent retention of initial strength. The recommended minimum acceptable M. D. fold retention after 24 days of ageing at 100° C as calculated from the regression line is 50%. This level of permanence, though very good, is quite achievable. (Table 3).

A paper with very good initial strength might lose more than 50% of its folding endurance and still be stronger longer than one which barely meets the specifications. See Figure 4. Since the real objective is to make paper useful for as long as possible, it is reasonable to accept any paper which does not reach the point of unusability earlier than one which meets the minimum standard. Barrow defined his "restoration category" as papers having three or fewer folds at 0.5 tension. If for the present purpose, papers in need of restoration are defined as those having one fold or less at 1 kg tension, it can be determined by extrapolation that a paper which meets the minimum specifications previously proposed would reach unusability in 118 days. Therefore the permanence specifications can be expanded to include any paper whose extrapolated regression line shows an M. D. fold of 1 or more after 118 days of ageing, providing that it also meets the initial folding endurance requirement.

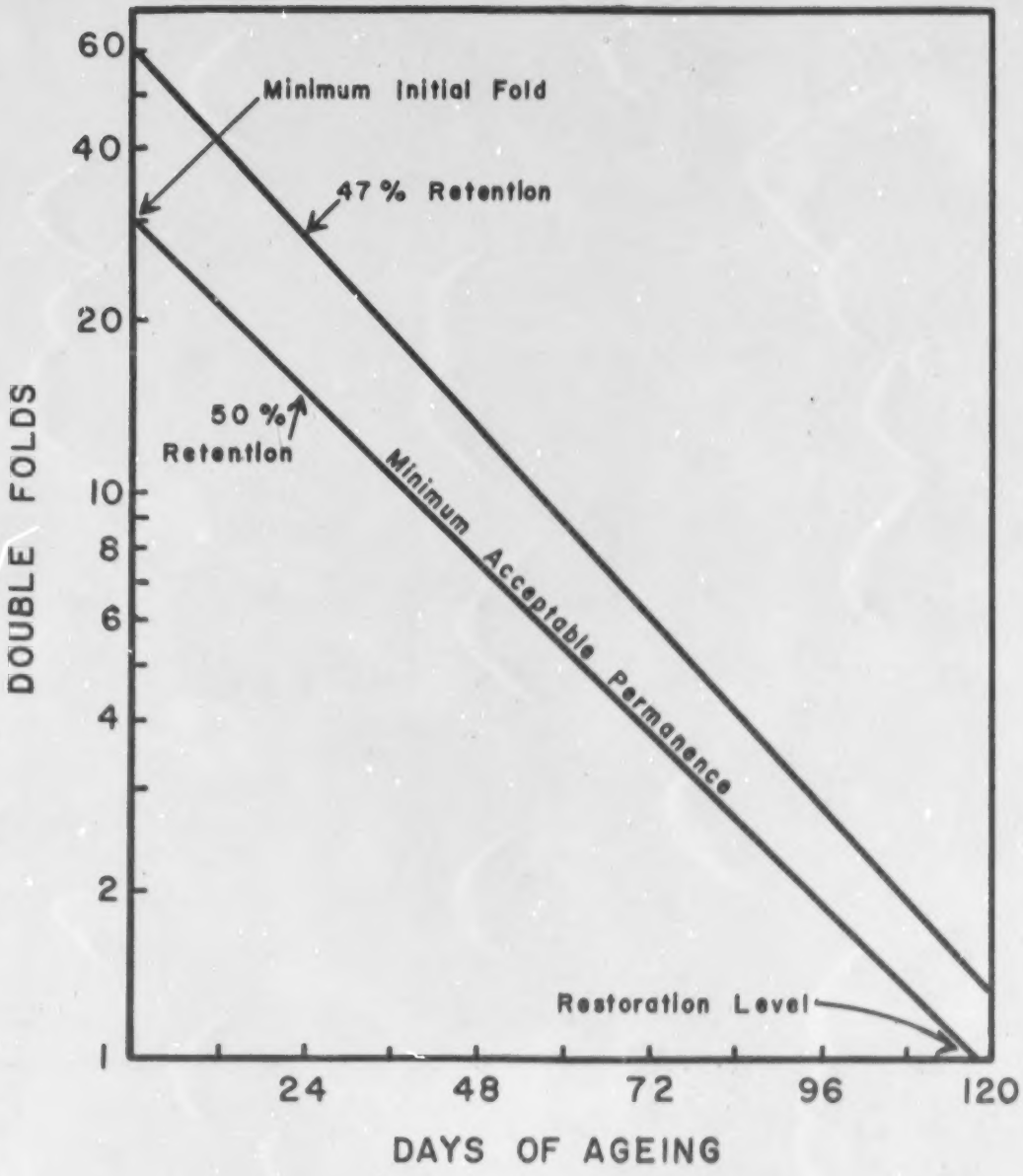

Figure 4 - A paper which retains less than 50% of its initial folding endurance after 24 days of ageing may be accepted if it will not reach the restoration level earlier than a paper which meets the minimum specifications.

If it is assumed that 3 days of ageing at 100° C. is equivalent to 25 years of natural ageing, a paper meeting this minimum strength retention requirement could be expected to need restoration in 983 years if it is not handled. In normal careful use, it should last 500 years, satisfying the longevity requirement in the definition of permanent/durable paper given in Part I of this report. If a higher natural ageing equivalency is accepted for 3 days of accelerated ageing, service life of paper will be increased proportionally.

Obviously, some of the papers tested can meet some of the proposed specifications, but there are 8 which can meet all of them. They are Papers #112 (80 lb.), #114 (70 lb.), #125 (63 lb.), #115, #124 (60 lbs.), #101 (50 lb.), and #102, #103 (40 lb.). (Tables 3, 20). Thus papers of this quality are not only desirable but possible.

1973 Specifications for Permanent/Durable Uncoated Book Paper

A. Minimum cold extraction pH of 7.5 (TAPPI method T-435).

B. Minimum C. D. folding endurance of 30 at 1 kg tension (MIT, 25 replicates, TAPPI method T-511).

C. Minimum M. D. tear resistance (Elmendorf, ten replicate 8-ply tears, TAPPI method T-414) of 70 grams for 60 lb. (25"x 38" - 500) paper and proportionally more for heavier weights. For lighter weights:

Basis Weight	Minimum Acceptable M. D. Tear
40	40.0 gm
45	47.5
50	55.0
55	62.5

D. Minimum retention of M. D. folding endurance after 24 days of ageing at 100° C in a forced circulation oven (as calculated from a six-point regression line) of 50% or M. D. folding endurance of one or more after 118 days of ageing as determined by extrapolation.

Submitted by the W. J. Barrow Research Laboratory, Inc. to the Library of Congress and the Council on Library Resources, March 22, 1973.

Table 1

Commercial Papers Tested

Paper	pH	Rosin	Carbonate	Fiber
101	9.5	N	P	
102	9.4	N	P	SW, HW Sulfate
103	9.5	N	P	SW, HW Sulfate
104	8.9	N	P	SW, HW Sulfate
105	9.2	N	P	SW, HW Sulfate
106	7.7	N	N	Contains Sulfate
107	7.4	P	N	Contains Sulfate
108	7.5	P	N	SW, HW Sulfate; HW Sulfite
109	5.6	P	N	SW, HW Sulfate; HW Sulfite
110	8.0	P	P	SW, HW Sulfate; HW Sulfite
111	7.8	P	P	SW, HW Sulfate; HW Sulfite
112	9.2	N	P	SW, HW Sulfate
113	9.0	N	P	SW, HW Sulfate
114	6.9	N	N	Woodpulp
115	8.4	N	P	SW, HW Sulfate
116	8.2	N	P	
117	8.6	N	P	
118	7.0	P	P	
119	7.3	P	P	
120	6.6	P	P	
121	8.5	N	P	
122	8.7	N	P	
123	8.7	N	P	HW, SW
124	9.2	N	P	
125	8.2	N	N	Cotton
126	6.8	N	N	Sulfate
127	5.6	P	N	60% deinked fiber
128	7.2	P (?)	N	Reclaimed chemical wood
129	6.4	P (?)	N	
130	5.6	P	N	
131	8.8	N	P	
132	7.7	N	N	SW, HW Sulfate; HW sulfite

Table 2

Folding Endurance (MIT, 1.0 kg tension, avg. of 50 tests), Tear Resistance (avg. of ten 8-ply tears) and pH of Papers Aged at 100° C

Paper	Test		Days at 100° C 0	6	12	18	24	30
101	Fold	MD	80	66	60	60	55	52
		CD	38	37	35	37	29	30
	Tear	MD	71.6	68.8	66.7	63.4	62.7	61.0
		CD	79.0	74.6	73.7	70.0	69.7	68.5
	pH		9.4	9.4	9.3	9.2	9.2	9.2
102	Fold	MD	303	272	274	241	158	156
		CD	90	79	63	58	59	47
	Tear	MD	40.2	37.3	39.4	35.2	35.1	33.5
		CD	43.2	40.3	41.2	37.9	37.8	34.5
	pH		9.4	9.3	9.2	9.2	9.1	9.0
103	Fold	MD	266	293	297	238	234	191
		CD	38	38	31	37	34	26
	Tear	MD	41.7	38.2	40.0	36.9	37.9	34.6
		CD	48.5	45.5	46.6	44.0	44.1	39.8
	pH		9.5	9.4	9.3	9.2	9.2	9.0
104	Fold	MD	19	16	12	13	11	7
		CD	23	21	19	17	17	14
	Tear	MD	73.7	69.0	67.2	64.7	64.8	59.2
		CD	65.4	65.4	63.2	58.6	57.3	52.2
	pH		8.9	8.8	8.8	8.8	8.7	8.5

Table 2 (continued)

Folding Endurance (MIT, 1.0 kg tension, avg. of 50 tests), Tear Resistance (avg. of ten 8-ply tears) and pH of Papers Aged at 100° C.

Paper	Test		Days at 100° C 0	6	12	18	24	30
105	Fold	MD	170	112	95	70	53	35
		CD	130	89	73	58	44	35
	Tear	MD	42.3	41.8	39.4	36.3	35.2	34.9
		CD	42.2	42.0	39.7	37.2	36.2	35.7
	pH		9.2	8.9	8.7	8.6	8.5	8.4
106	Fold	MD	308	274	250	235	202	184
		CD	58	53	50	48	43	38
	Tear	MD	46.9	44.6	44.2	43.4	40.4	40.5
		CD	52.5	51.6	50.5	50.7	48.1	46.3
	pH		7.7	7.0	6.8	6.7	6.8	6.7
107	Fold	MD	134	89	75	62	51	42
		CD	78	48	44	41	33	29
	Tear	MD	40.6	38.6	36.5	36.6	34.7	33.5
		CD	45.6	42.0	41.8	41.7	38.1	36.1
	pH		7.4	7.1	7.0	7.0	7.0	6.9
108	Fold	MD	20	12	9	8	5	4
		CD	26	17	14	12	10	10
	Tear	MD	66.6	59.3	55.9	55.6	53.2	49.3
		CD	55.4	47.3	45.5	43.9	41.1	38.6
	pH		7.5	7.1	6.8	6.5	6.7	6.5

Table 2 (continued)

Folding Endurance (MIT, 1.0 kg tension, avg. of 50 tests), Tear Resistance (avg. of ten 8-ply tears) and pH of Papers Aged at 100° C

Paper	Test		Days at 100° C 0	6	12	18	24	30
109	Fold	MD	35	13	5	2	1	1
		CD	10	5	3	2	1	1
	Tear	MD	48.5	43.8	31.8	27.0	25.3	19.8
		CD	61.1	48.4	40.6	36.4	32.2	28.0
	pH		6.2	5.6	5.4	5.2	5.3	5.1
110	Fold	MD	37	17	9	5	5	2
		CD	7	5	3	3	2	1
	Tear	MD	52.6	41.4	35.9	32.3	30.4	27.0
		CD	68.2	55.6	48.0	45.0	42.1	39.0
	pH		8.0	7.8	7.7	7.7	7.7	7.7
111	Fold	MD	15	10	6	5	4	3
		CD	7	6	5	4	3	3
	Tear	MD	42.4	35.7	30.7	28.0	25.0	24.6
		CD	50.6	42.0	38.5	33.4	32.3	30.5
	pH		7.8	7.6	7.6	7.6	7.5	7.4
112	Fold	MD	678	565	560	491	495	488
		CD	239	226	229	183	182	164
	*Tear	MD	156.1	149.2	146.8	146.7	142.7	136.3
	*	CD	169.4	160.8	157.8	157.0	152.7	148.6
	pH		9.2	8.8	8.8	8.8	8.8	8.7

*Average of 20 four-ply tears.

Table 2 (continued)

Folding Endurance (MIT, 1.0 kg tension, avg. of 50 tests), Tear Resistance (avg. of ten 8-ply tears) and pH of Papers Aged at 100° C

Paper	Test		0	6	12	18	24	30
113	Fold	MD	23	17	18	16	14	11
		CD	21	18	18	17	15	14
	Tear	MD	74.6	68.7	67.0	64.2	64.5	62.6
		CD	72.2	66.3	64.2	61.5	61.0	60.1
	pH		9.0	8.9	8.9	8.7	8.7	8.7
114	Fold	MD	284	217	177	140	96	77
		CD	69	58	47	40	32	26
	Tear	MD	85.9	81.9	78.3	74.8	71.0	68.5
		CD	101.6	95.2	91.7	88.2	85.3	82.5
	pH		6.9	6.7	6.6	6.5	6.4	6.4
115	Fold	MD	171	155	112	114	92	92
		CD	45	43	35	35	35	30
	Tear	MD	74.1	70.6	65.3	65.1	64.8	62.9
		CD	81.2	77.2	72.7	70.2	71.0	69.5
	pH		8.4	8.3	8.1	8.1	8.1	8.1
116	Fold	MD	21	13	8	9	8	6
		CD	11	9	11	7	6	6
	Tear	MD	55.4	53.6	48.0	47.8	44.9	44.4
		CD	61.9	55.4	52.7	48.6	47.5	47.7
	pH		8.2	8.0	8.0	7.8	7.8	7.7

Table 2 (continued)

Folding Endurance (MIT, 1.0 kg tension, avg. of 50 tests), Tear Resistance (avg. of ten 8-ply tears) and pH of Paper Aged at 100° C

Paper	Test		Days at 100° C 0	6	12	18	24	30
117	Fold	MD	41	30	24	22	19	16
		CD	17	13	12	11	10	9
	Tear	MD	43.0	42.1	38.6	36.9	36.6	35.4
		CD	47.0	44.6	41.4	39.6	39.5	38.4
	pH		8.6	8.1	8.1	8.2	8.1	8.1
118	Fold	MD	10	7	5	4	4	3
		CD	6	5	4	4	3	3
	Tear	MD	45.8	39.5	36.7	34.2	34.0	31.2
		CD	51.2	44.6	41.6	38.3	37.1	34.6
	pH		7.0	6.9	6.9	6.9	6.8	6.8
119	Fold	MD	20	13	10	8	3	4
		CD	10	7	7	6	5	4
	Tear	MD	54.9	48.8	43.3	39.3	40.2	34.9
		CD	58.2	52.6	46.6	46.1	44.3	40.9
	pH		7.3	7.1	6.8	6.7	6.7	6.7
120	Fold	MD	6	4	3	3	2	1.5
		CD	3	3	2	2	2	1.5
	Tear	MD	53.3	43.5	41.4	41.2	36.8	36.1
		CD	55.8	50.4	45.6	43.7	40.9	39.1
	pH		6.6	6.4	6.4	6.5	6.5	6.6

Table 2 (continued)

Folding Endurance (MIT, 1.0 kg tension, avg. of 50 tests), Tear Resistance (avg. of ten 8-ply tears) and pH of Papers Aged at 100° C

Paper	Test		0	6	12	18	24	30
121	Fold	MD	67	37	31	25	30	20
		CD	34	26	23	21	18	19
	Tear	MD	49.2	46.8	44.0	43.2	43.4	40.5
		CD	51.2	47.9	45.6	45.8	45.6	42.1
	pH		8.5	8.0	7.8	7.8	7.7	7.6
122	Fold	MD	49	36	28	27	23	20
		CD	9	7	6	6	6	6
	Tear	MD	49.2	46.0	44.4	42.4	42.1	39.5
		CD	56.3	53.4	48.5	48.4	46.6	45.4
	pH		8.7	8.6	8.5	8.5	8.5	8.3
123	Fold	MD	72	53	46	37	36	22
		CD	27	24	21	21	19	14
	Tear	MD	77.3	74.5	72.4	74.0	66.3	59.3
		CD	79.5	77.0	76.2	69.2	70.2	62.0
	pH		8.7	8.3	8.3	8.0	7.9	7.9
124	Fold	MD	238	206	202	171	152	146
		CD	74	70	64	56	58	58
	Tear	MD	80.1	78.0	80.2	75.5	74.1	72.9
		CD	86.7	86.8	88.6	84.7	80.8	79.7
	pH		9.2	9.0	8.9	8.8	8.8	8.7

Table 2 (continued)

Folding Endurance (MIT, 1.0 kg tension, avg. of 50 tests), Tear Resistance (avg. of ten 8-ply tears) and pH of Papers Aged at 100° C

Paper	Test		0	6	12	18	24	30
125	Fold	MD	423	348	313	269	182	158
		CD	156	147	136	123	97	88
	Tear	MD	88.0	82.8	79.8	73.2	72.5	70.4
		CD	91.2	85.6	82.4	81.2	77.4	73.6
	pH		8.2	7.9	7.6	7.4	7.4	7.4
126	Fold	MD	206	165	152	134	86	87
		CD	45	35	35	30	27	24
	Tear	MD	62.2	59.0	57.7	56.8	53.8	52.4
		CD	72.9	69.4	67.3	66.2	63.9	62.0
	pH		6.8	6.5	6.4	6.3	6.2	6.0
127	Fold	MD	24	13	8	6	4	3
		CD	15	9	7	7	4	3
	Tear	MD	67.7	57.8	51.3	48.7	43.2	38.4
		CD	68.5	59.1	52.2	48.4	44.5	37.9
	pH		5.6	5.4	5.2	5.1	5.0	4.9
128	Fold	MD	124	73	56	39	32	27
		CD	34	23	18	17	13	11
	Tear	MD	65.9	57.5	54.5	50.6	48.2	46.6
		CD	77.1	68.9	64.2	62.5	57.7	57.2
	pH		7.2	6.6	6.8	6.2	6.4	6.6

Table 2 (continued)

Folding Endurance (MIT, 1.0 kg tension, avg. of 50 tests), Tear Resistance (avg. of ten 8-ply tears) and pH of Papers Aged at 100° C

Paper	Test		Days at 100° C 0	6	12	18	24	30
129	Fold	MD	28	21	18	15	15	11
		CD	9	8	7	7	7	6
	Tear	MD	71.5	65.2	61.8	61.4	60.1	54.4
		CD	84.1	78.1	75.8	72.8	70.8	65.7
	pH		6.4	6.1	5.8	5.8	5.8	5.8
130	Fold	MD	31	17	11	9	6	4
		CD	10	6	5	4	4	3
	Tear	MD	42.9	37.9	35.3	33.2	31.6	28.3
		CD	52.5	46.8	42.9	40.9	39.4	34.3
	pH		7.0	5.6	5.5	5.4	5.2	5.2
131	Fold	MD	29	28	25	20	19	19
		CD	17	16	15	14	14	14
	Tear	MD	55.0	53.6	51.7	50.5	49.4	48.3
		CD	59.4	58.2	56.8	56.1	54.4	53.0
	pH		8.8	8.7	8.6	8.6	8.4	8.5
132	Fold	MD	427	325	328	261	282	247
		CD	263	254	245	215	205	176
	Tear	MD	45.6	44.3	41.8	39.3	38.8	36.7
		CD	44.2	42.2	43.7	40.1	41.4	38.4
	pH		7.7	7.1	6.8	6.7	6.5	6.4

Evaluation of Papers for Permanence and Durability

Paper	Weight	pH	Percentage retention of original strength after ageing 24 days @ 100°C					Initial Strength					
				Fold Endurance		Tear Resistance		Fold Endurance			Tear Resistance		
								M.D.	C.D.		M.D.		C.D.
			Rank*	M.D.	C.D.	M.D.	C.D.		Rank	Folds	Tear	Rank	
101	50 lb.	9.5	3	73	82	88	89	80	13	38	71.6	9	79.0
102	40 lb.	9.4	10	56	62	87	85	303	5	90	40.2	31	43.2
103	40 lb.	9.5	2	75	79	89	88	266	12	38	41.7	29	48.5
104	60 lb.	8.9	11	53	70	86	83	19	18	23	73.7	8	65.4
105	57 lb.	9.2	25	30	36	84	86	170	4	1 30	42.3	28	42.2
106	45 lb.	7.7	7	67	74	89	91	308	9	58	46.9	23	52.5
107	45 lb.	7.4	20	41	49	86	85	134	6	78	40.6	30	45.6
108	60 lb.	7.5	26	28	50	81	77	20	17	26	66.6	13	55.4
109	60 lb.	5.6	32	4	11	49	55	35	24	10	48.5	22	61.1
110	61 lb.	8.0	31	11	24	61	66	37	29	7	52.6	19	68.2
111	50 lb.	7.8	27	28	47	64	67	15	30	7	42.4	27	50.6
112	80 lb.	9.2	1	78	73	91	91	678	2	239	156.1	1	169.4
113	60 lb.	9.0	9	59	71	88	87	23	19	21	74.6	6	72.2

Evaluation of Papers for Permanence and Durability

Paper	Weight	pH	Percentage retention of original strength after ageing 24 days @ 100°C					Initial Strength					
				Fold Endurance		Tear Resistance		Fold Endurance			Tear Resistance		
			Rank*	M.D.	C.D.	M.D.	C.D.	M.D.	C.D.		M.D.		C.D.
									Rank	Folds	Tear	Rank	
114	70 lb.	6.9	22	35	46	83	85	284	8	69	85.9	4	101.6
115	60 lb.	8.4	8	59	75	88	89	171	11	45	74.1	17	81.2
116	60 lb.	8.2	19	41	64	83	81	21	23	11	55.4	15	61.9
117	50 lb.	8.6	13	51	62	85	85	41	20	17	43.0	25	47.0
118	60 lb.	7.0	21	40	56	76	74	10	31	6	45.8	24	51.2
119	60 lb.	7.3	28	23	52	71	77	20	26	10	54.9	17	58.2
120	60 lb.	6.6	23	33	67	75	76	6	32	3	53.3	18	55.8
121	60 lb.	8.5	17	45	61	87	88	67	15	34	49.2	21	51.2
122	50 lb.	8.7	12	52	75	85	84	49	27	9	49.2	20	56.3
123	57 lb.	8.7	18	43	63	83	83	72	16	27	77.3	5	79.5
124	60 lb.	9.2	6	67	77	92	93	238	7	74	80.1	3	86.7

Table 3 (continued)

Evaluation of Papers for Permanence and Durability

Paper	Weight	pH	Percentage retention of original strength after ageing 24 days @ 100° C					Initial Strength					
				Fold Endurance		Tear Resistance		Fold Endurance			Tear Resistance		
			Rank*	M.D.	C.D.	M.D.	C.D.	M.D.	C.D. Rank	C.D. Folds	M.D. Tear	M.D. Rank	C.D.
125	63 lb.	8.2	16	45	62	83	85	423	3	156	88.0	2	91.2
126	51 lb.	6.8	15	48	63	88	88	206	10	45	62.2	14	72.9
127	50 lb.	5.6	30	19	29	65	64	24	22	15	67.7	11	68.5
128	60 lb.	7.2	24	30	42	77	79	124	14	34	65.9	13	77.1
129	60 lb.	6.4	14	50	78	83	84	28	28	9	71.5	10	84.1
130	60 lb.	5.6	29	22	50	74	74	31	25	10	42.9	26	52.5
131	60 lb.	8.8	4	69	82	90	91	29	21	17	55.0	16	59.4
132	45 lb.	7.7	5	68	73	84	91	427	1	263	45.6	25	44.2

*Ranked according to M.D. folding endurance retention.

Table 4

Comparison of Lasting Qualities of 60 lb. Papers

	Paper	Ranks			
		MD Fold Retention	CD Fold	MD Tear	Sum
1	124	6	7	3	16
2	125	16	3	2	21
3	115	8	11	7	26
4	113	9	19	6	34
5	104	11	18	8	37
6	123	18	16	5	39
7	131	4	21	16	41
8	128	24	14	13	51
9	129	14	28	10	52
10	121	17	15	21	53
11	108	26	17	12	55
12	116	19	23	15	57
13	105	25	4	28	57
14	127	30	22	11	63
15	119	28	26	17	71
16	120	23	32	18	73
17	118	21	31	24	76
18	109	32	24	22	78
19	110	31	29	19	79
20	130	29	25	26	80

Table 5

Retention of Original Strength after Ageing 24 Days at 100° C

Paper	% MD Fold		MD Tear	
	Rank	Retention	Rank	Retention
112	1	78	2	91
103	2	75	4	89
101	3	73	6	88
131	4	69	3	90
132	5	68	16	84
124	6	67	1	92
106	7	67	5	89
115	8	59	7	88
113	9	59	8	88
102	10	56	10	87
104	11	53	12	86
122	12	52	14	85
117	13	51	15	85
129	14	50	18	83
126	15	48	9	88
125	16	45	19	83
121	17	45	11	87
123	18	43	20	83
116	19	41	21	83
107	20	41	13	86
118	21	40	25	76
114	22	35	22	83
120	23	33	26	75
128	24	30	24	77
105	25	30	17	84
108	26	28	23	81
111	27	28	30	64
119	28	23	28	71
130	29	22	27	74
127	30	19	29	65
110	31	11	31	61
109	32	4	32	49

Table 6

Effect of Relative Humidity on the Deterioration Rate of Paper #115

Relative Humidity	Test		Days of Ageing 0	18	36	54	72	90
20%	Fold	MD	163	123	134	127	108	116
		CD	50	48	53	55	47	48
	Tear	MD	72.9	72.8	69.0	69.3	66.9	67.8
		CD	77.5	75.4	73.7	71.7	73.0	71.3
	pH		9.1	9.0	9.0	9.0	9.1	9.0
35%	Fold	MD	171	133	122	127	113	100
		CD	54	50	53	51	44	46
	Tear	MD	75.7	74.3	69.9	68.9	66.9	64.6
		CD	78.5	75.0	73.6	71.2	70.2	68.2
	pH		8.2	8.0	7.8	7.9	7.9	7.9
50%	Fold	MD	167	143	122	103	96	84
		CD	54	53	45	49	37	36
	Tear	MD	71.4	71.8	66.7	65.9	64.3	64.7
		CD	77.1	74.6	70.7	70.7	69.3	69.4
	pH		8.5	8.6	8.5	8.5	8.6	8.6
65%	Fold	MD	171	131	115	85	89	71
		CD	45	38	35	35	34	26
	Tear	MD	74.1	69.8	66.4	68.6	64.4	61.1
		CD	81.2	76.7	73.2	71.6	70.2	64.2
	pH		8.4	8.9	8.7	8.6	8.6	8.6

Table 7

Effect of Relative Humidity on the Deterioration Rate of Paper #116

Relative Humidity	Test		Days of Ageing 0	18	36	54	72	90
20%	Fold	MD	18	16	15	14	11	11
		CD	11	11	10	10	8	8
	Tear	MD	54.3	53.0	50.2	51.3	49.3	49.0
		CD	57.6	58.8	56.2	51.5	54.2	53.2
	pH		8.7	8.5	8.4	8.5	8.4	8.4
35%	Fold	MD	23	10	13	13	12	9
		CD	11	18	10	9	8	7
	Tear	MD	57.6	54.8	51.7	48.2	49.4	43.7
		CD	60.3	56.2	54.0	51.4	51.9	48.2
	pH		7.8	7.7	7.5	7.4	7.5	7.5
50%	Fold	MD	21	15	10	9	8	8
		CD	12	10	8	8	7	7
	Tear	MD	57.0	51.1	50.2	47.0	45.8	46.2
		CD	57.4	51.6	51.2	49.2	50.4	47.8
	pH		8.1	8.1	7.9	8.0	7.9	7.9
65%	Fold	MD	21	14	14	11	10	9
		CD	11	9	8	8	8	6
	Tear	MD	55.4	52.8	51.0	48.8	47.7	46.5
		CD	61.9	58.5	53.0	51.8	50.5	46.0
	pH		8.2	8.4	8.3	8.3	8.2	8.1

Table 8

Percent Retention of Original Strength of Papers Aged 90 Days at 76° C and Four Relative Humidities

Paper	Folding Endurance							
	MD				CD			
	20%	35%	50%	65%	20%	35%	50%	65%
#115	73	64	50	44	96	83	64	64
#116	61	53	39	47	73	50	55	60
	Tear Resistance							
#115	86	85	89	85	92	88	90	81
#116	90	71	82	84	90	82	86	76

Table 9

Comparison of Folding Endurance, Tear Resistance and Thickness of Papers in Different Weights

Paper	Nominal Basis Wt.	Calculated Basis Wt.	Thickness	Fold		Tear	
				MD	CD	MD	CD
101	50	51.2	.0043"	125	40	66.3	76.4
	70	71.0	.0049	291	183	91.9	94.7
104	50	51.6	.0046	13	22	56.1	48.4
	60	60.9	.0052	19	23	70.6	66.3
	70	70.9	.0066	14	10	87.9	86.2
115	50	51.0	.0042	101	43	54.3	57.2
	60	57.6	.0049	117	57	69.2	75.9
	70	71.2	.0061	93	38	93.1	103.7
116	50	52.0	.0043	47	13	47.0	54.2
	60	59.6	.0051	19	12	56.1	59.9
	70	70.2	.0060	36	18	77.6	81.7
118	50	49.4	.0035	13	9	35.9	39.8
	60	58.6	.0042	10	7	44.4	51.0
	70	71.8	.0052	9	6	58.3	65.9

Table 10

Relation of Basis Weight, Thickness and Tear Resistance

ber	Nominal Basis Wt.	Calculated Basis Wt.	% Increase	Thickness	% Increase	Tear Resistance MD	% Increase	CD	% Increase
1	50	52.2		.0043"		66.3		76.4	
			36		14		39		24
	70	71.0		.0049		9 1.9		9 4.7	
4	50	51.6		.0046		56.1		48.4	
			18		13		26		37
	60	60.9		.0052		70.6		66.3	
			16		27		25		30
	70	70.9		.0066		87.9		86.2	
5	50	51.0		.0042		54.3		57.2	
			13		17		27		33
	60	57.6		.0049		69.2		75.9	
			24		24		35		37
	70	71.2		.0061		93.1		103.7	
6	50	52.0		.0043		47.0		54.2	
			15		17		19		11
	60	59.6		.005 1		56.1		59.9	
			18		18		38		36
	70	70.2		.0060		77.6		81.7	
8	50	49.4		.0035		35.9		39.8	
			19		20		24		28
	60	58.6		.0042		44.4		51.0	
			23		24		31		29
	70	71.8		.0052		58.3		65.9	

Table 11

Fold Testing of Five Papers Under Different Arrangements of the MIT Tester

Mode of Test	Paper Number 104	105	115	116	118
1 kg. tension, no fan	24	218	145	22	11
1 kg. tension, with fan	22	173	148	23	11
.5 kg. tension, with fan	370	2309	2185	407	139
.5 kg. tension, no fan	292	2051	1666	371	126
1 kg. spring tension	24	183	117	19	12
.5 kg. spring tension	266	1924	1508	332	103
1 kg. tension, first fold to wire side	24	202	135	24	11
.5 kg. tension, first fold to wire side	311	2192	1650	355	132

Except where indicated, the blower is used, tension is provided by dead weight and the first fold is toward the felt side.

Table 12

Comparison of MIT Folding Endurance Data (MD)
for Tests Run with Spring Scale and Dead Weight

	1 kg. tension		.5 kg. tension	
	Spring Scale	Dead Wt.	Spring Scale	Dead Wt.
Paper #104				
Mean	24	22	266	370
Median	23	21	258.5	359.5
Extreme values	7-48	10-46	103-497	154-849
Range	41	36	394	695
Standard deviation	7.66	7.83	79.69	121.80
Coefficient of variation	32%	33%	33%	30%
Paper #105				
Mean	183	173	1924	2309
Median	175	166	1924.5	2323
Extreme values	41-358	41-386	685-3047	1010-3640
Range	317	345	2362	2630
Standard deviation	66.26	66.42	444.8	486.06
Coefficient of variation	36%	38%	23%	21%
Paper #115				
Mean	117	148	1508	2185
Median	117	146	1562.5	2138
Extreme values	48-205	62-290	649-2350	821-3254
Range	157	228	1701	2433
Standard deviation	33.13	43.33	368.95	472.41
Coefficient of variation	28%	29%	24%	22%
Paper #116				
Mean	19	23	332	407
Median	18	22	328.5	389
Extreme values	6-37	12-50	108-668	123-806
Range	31	38	560	683
Standard deviation	5.64	7.30	123.48	142.93
Coefficient of variation	30%	32%	37%	35%
Paper #118				
Mean	12	11	103	139
Median	11	11	106.5	136.5
Extreme values	7-17	7-17	33-172	66-218
Range	10	10	139	152
Standard deviation	2.06	1.50	28.54	33.75
Coefficient of variation	17%	14%	28%	24%

$$\text{Coefficient of Variation} = \frac{\text{Standard Deviation}}{\text{Mean}} \cdot 100$$

Table 13

Comparison of Folding Endurance at 1.0 kg. and .5 kg. Tension

	Paper Number				
	104	105	115	116	118
Blower, dead weight, 1st fold to felt side					
.5 kg. tension	370	2309	2185	407	139
1.0 kg. tension	22	173	148	23	11
Ratio	16.8	13.3	14.8	17.7	12.6
Blower, dead weight, 1st fold to wire side					
.5 kg. tension	311	2192	1650	355	132
1.0 kg. tension	24	202	135	24	11
Ratio	13.0	10.9	12.2	14.8	12.0
Blower, spring scale, 1st fold to felt side					
.5 kg. tension	266	1924	1508	332	103
1.0 kg. tension	24	183	117	19	12
Ratio	11.1	10.5	12.9	17.5	8.6
No blower, dead weight, 1st fold to felt side					
.5 kg. tension	292	2051	1666	371	126
1.0 kg. tension	24	218	145	22	11
Ratio	12.2	9.4	11.5	16.9	11.5

Table 14

Comparison of MIT Folding Endurance Data (MD) for Tests Run with and without Fan

	1 kg. tension		.5 kg. tension	
	With Fan	Without Fan	With Fan	Without Fan
Paper #104				
Mean	22	24	370	292
Median	21	23	359.5	281
Extreme values	10-46	12-61	154-849	116-535
Range	36	49	695	419
Standard deviation	7.83	7.66	121.80	93.00
Coefficient of variation	33%	32%	30%	32%
Paper #105				
Mean	173	218	2309	2051
Median	166	214	2323	2077.5
Extreme values	41-386	67-389	1010-3640	909-3595
Range	345	322	2630	2686
Standard deviation	66.42	72.46	486.06	500.10
Coefficient of variation	38%	33%	21%	24%
Paper #115				
Mean	148	145	2185	1660
Median	146	137	2138	1652
Extreme values	62-290	68-287	821-3254	859-4151
Range	228	219	2433	3292
Standard deviation	43.33	45.42	472.41	391.19
Coefficient of variation	29%	31%	22%	23%
Paper #116				
Mean	23	22	407	371
Median	22	21.5	389	349.5
Extreme values	12-50	10-36	123-806	143-769
Range	38	26	683	626
Standard deviation	7.30	5.57	142.93	108.73
Coefficient of variation	32%	25%	35%	29%
Paper #118				
Mean	11	11	139	126
Median	11	11	136.5	129
Extreme values	7-17	7-17	66-218	23-227
Range	10	10	152	204
Standard deviation	1.50	1.88	33.75	38.36
Coefficient of variation	14%	17%	24%	30%

$$\text{Coefficient of Variation} = \frac{\text{Standard Deviation}}{\text{Mean}} \cdot 100$$

Table 15

Comparison of MIT Folding Endurance Data (MD) for Tests in which the First Fold was to the Felt Side and to the Wire Side

First fold to:	1 kg. tension		.5 kg. tension	
	Felt Side	Wire Side	Felt Side	Wire Side
Paper #104				
Mean	22	24	370	311
Median	21	24	359.5	312
Extreme Values	10-46	12-47	154-849	83-542
Range	36	35	695	459
Standard Deviation	7.83	5.72	121.80	99.36
Coefficient of Variation	33%	24%	30%	32%
Paper #105				
Mean	173	202	2309	2192
Median	166	189	2323	2209.5
Extreme Values	41-386	35-392	1010-3640	935-3110
Range	345	357	2630	2175
Standard Deviation	66.42	73.48	486.06	453.83
Coefficient of Variation	38%	36%	21%	21%
Paper #115				
Mean	148	135	2185	1650
Median	146	133	2138	1655.5
Extreme Values	62-290	54-263	821-3254	472-2344
Range	228	209	2433	1872
Standard Deviation	43.33	38.05	472.41	317.64
Coefficient of Variation	29%	28%	22%	19%
Paper #116				
Mean	23	24	407	355
Median	22	22	389	358
Extreme Values	12-50	12-46	123-806	81-641
Range	38	34	683	560
Standard Deviation	7.30	7.22	142.93	111.36
Coefficient of Variation	32%	30%	35%	31%
Paper #118				
Mean	11	11	139	132
Median	11	11	136.5	127
Extreme Values	7-17	6-15	66-218	41-244
Range	10	9	152	203
Standard Deviation	1.50	1.68	33.75	40.40
Coefficient of Variation	14%	15%	24%	31%

$$\text{Coefficient of Variation} = \frac{\text{Standard Deviation}}{\text{Mean}} \cdot 100$$

Table 16

Effect of Radius of Curvature of Folding Edges of the MIT Tester on Folding Endurance Values

Paper	Test Direction	Radius of Curvature .012"	.015"	.018"
104	MD	16	22	24
	CD	20	23	27
105	MD	127	230	276
	CD	100	152	293
115	MD	120	174	209
	CD	42	43	56
116	MD	17	19	28
	CD	10	11	14
118	MD	9	11	13
	CD	6	6	8

Table 17

Folding Endurance Obtained with out-of-specification Folding Edges Expressed as a Percentage of the Value Obtained with Standard (.015") Edges

Paper	Test Direction	Radius of Curvature .012"	.018"
104	MD	73%	109
	CD	87	117
105	MD	55	120
	CD	66	193
115	MD	69	120
	CD	98	130
116	MD	89	147
	CD	91	127
118	MD	82	118
	CD	100	133

Table 18

CD Folding Endurance of 60 lb. Papers

Paper	Overall Rank	60 lb. Rank	Fold
125	3	1	156
105	4	2	130
124	7	3	74
115	11	4	45
128	14	5	34
121	15	6	34
123	16	7	27
108	17	8	26
104	18	9	23
113	19	10	21
131	21	11	17
127	22	12	15
116	23	13	11
109	24	14	10
130	25	15	10
119	26	16	10
129	28	17	9
110	29	18	7
118	31	19	6
120	32	20	3

Table 19

MD Tear Resistance of 60 lb. Papers

Paper	Overall Rank	60 lb. Rank	Tear
125	2	1	88.0
124	3	2	80.1
123	5	3	77.3
113	6	4	74.6
115	7	5	74.1
104	8	6	73.7
129	10	7	71.5
127	11	8	67.7
108	12	9	66.6
128	13	10	65.9
116	15	11	55.4
131	16	12	55.0
119	17	13	54.9
120	18	14	53.3
110	19	15	52.6
121	21	16	49.2
109	22	17	48.5
118	24	18	45.8
130	26	19	42.9
105	28	20	42.3

Table 20

Folding Endurance, Tear Resistance and Folding Endurance Retention of Papers having Basis Weights other than 60 lb.

Paper	Weight	MD Fold Retention	CD Fold	MD Tear	Minimum Acceptable Tear
102	40	56	90	40.2	40.0
103	40	75	38	41.7	40.0
106	45	67	58	46.9	47.5
107	45	41	78	40.6	47.5
132	45	68	263	45.6	47.5
101	50	73	38	71.6	55.0
111	50	28	7	42.4	55.0
117	50	51	17	43.0	55.0
122	50	52	9	49.2	55.0
126	51	48	45	62.2	55.0
114	70	35	69	85.9	81.7
112	80	78	239	156.1	93.3

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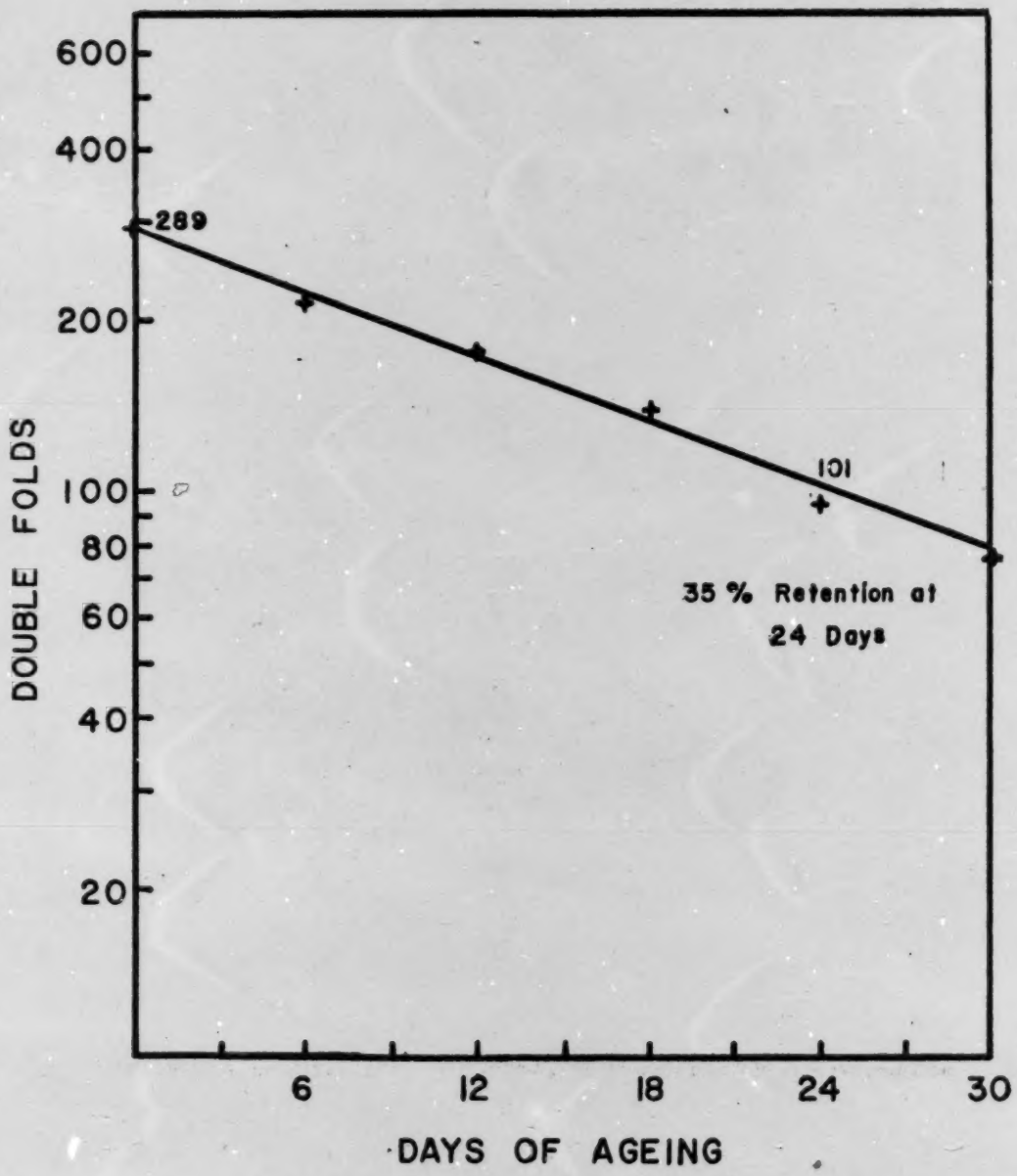

Figure 5 - Machine Direction Folding Endurance of Paper 114 at 100°C